THE MEASUREMENT AND PARTIAL EXPLANATION OF THE EFFECT OF PRESSURE ON THE SPECIFIC ELECTRICAL CONDUCTANCE OF SEA WATER

by

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THESIS

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The Measurement and Partial Explanation of the Effect of Pressure on the Specific Electrical Conductance of Sea Water

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ABSTRACT

The increase in specific conductance of sea water with increased pressure was measured using two parcels of sea water (32.448 °/oo and 37.152 °/oo) at six temperatures from 2.39° C to 17.39° C. The pressure was incremented in steps of 140 decibars to a pressure of 4,000 decibars. Although the effect of pressure on the specific conductance of sea water is nearly linear, it must be described by a higher order polynomial if it is to be used to measure salinity to the usual accuracy required in oceanography. The three major effects that cause the increase in the specific conductance of sea water with increased pressure are shown to be: increased effective concentration due to compression, increased ionic mobility due to the breakdown of Frank-Wen clusters and the increased disassociation of magnesium sulphate ion pairs.

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ACKNOWLEDGMENT

This work would not have been possible without the advice and encouragement of Associate Professor C. F. Rowell of the Naval Postgraduate School.

The pressure vessel used was designed and built by Lieutenant M. E. Mays, USN. The apparatus was modified and maintained by the laboratory technicians from the Department of Material Science and Chemistry, Naval Postgraduate School.

The data was reduced and evaluated on the IBM-360 computer of the Naval Postgraduate School Computer Facility. The computer facility personnel provided valuable advice during this process.

I. INTRODUCTION

There are good grounds for expecting better correlation between conductivity and density than between chlorinity and density [Cox et al., 1962]. Consequently, salinity has been defined in terms of conductivity by UNESCO [International Oceanographic Tables, 1966].

Conductivity ratio is the ratio of the conductivity of a sample of sea water to that of sea water having a salinity of exactly 35 °/oo, both being at the same temperature and under a pressure of one standard atmosphere [International Oceanographic Tables, 1966]. This ratio is represented by $\frac{C(S, T_1, 0)}{C(35, T_1, 0)}$ where the pressure variable refers to "sea pressure" so that the zero denotes a pressure of one atmosphere. The salinity is measured in terms of the number of parts of dissolved salts in one thousand parts of sea water and is labeled "°/oo" or "ppt." The decibar has been used as the unit of pressure measurement since, in the ocean, the pressure in decibars is approximately equal, numerically, to the depth in meters.

Whenever it was necessary to convert salinity to chlorinity, the following was used:

$$\text{SALINITY} = 1.80655 \times \text{CHLORINITY}$$

A laboratory salinometer measures the conductivity ratio described above since it is calibrated several times daily using standard sea water of 35 °/oo [Brown and Hamon, 1961]. The

measured ratio is then converted to the ratio $\frac{C(S, 15, 0)}{C(35, 15, 0)}$ which defines salinity.

An in situ salinometer measures the ratio $\frac{C(S, T, P)}{C(35, 15, 0)}$, and a knowledge of both the temperature-conductivity effect and the pressure-conductivity effect is necessary to convert this to $\frac{C(S, 15, 0)}{C(35, 15, 0)}$. In situ salinometers have been described by Hamon [1955], Prichard [1959] and Siedler [1963]. The in situ salinometer requires very stable geometry in the sensing element as well as very stable electronics since most are calibrated infrequently.

The effect of pressure on the conductivity of sea water has been studied previously, but in view of its vital role in evaluating the data from an in situ salinometer, this investigation was undertaken to refine the previous results by taking data in small pressure increments.

II. PREVIOUS INVESTIGATIONS

A. EFFECTS AT ATMOSPHERIC PRESSURE

The specific conductance of sea water of various chlorinities was investigated by Thomas et al. [1934] over the temperature range 0° to 25° C. A table was prepared for converting from chlorinity to specific conductivity and vice versa; this represented the best available data for many years and was adequate for salinity determinations using inductive or conductive salinometers where the specific conductance of the sample is compared to that of a standard by forming a conductivity ratio.

Pollak [1954] has criticized the work of Thomas et al. because of errors from two possible sources.

First is the use of the results of Parker and Parker [1924] for the specific conductance of standard potassium chloride solutions to calibrate the conductivity cells. Jones and Bradshaw [1933] point out that the values of Parker and Parker are in error due to a capacitive effect between adjacent parts of the cell that were of opposite polarity. Jones and Bradshaw developed new values for the specific conductance of standard potassium chloride solutions.

Secondly, Thomas et al. also used conductivity cells (Washburn pipet type) that allowed a capacitive shunt (similar to that of Parker and Parker) that could produce errors. These two errors are of opposite sign and would cancel each other to some unknown extent.

The conductivity of very dilute solutions of sea water, such as would result from a distillation process, has been studied by Malmberg [1965].

Weyl [1964] has further analyzed the data of Thomas et al. and has developed a polynomial for evaluating the following differential:

$$\left[\frac{\partial \text{Sp. Conductance}}{\partial \text{Temp}}\right]_{\substack{\text{atmospheric} \\ \text{pressure}}} = \text{Fcn (Temp, Chlorinity)}$$

Weyl also has developed a polynomial for evaluating the following:

$$\left[\text{Sp. Conductance}\right]_{\substack{\text{atmospheric} \\ \text{pressure}}} = \text{Fcn (Temp, Chlorinity)}$$

Reeburgh [1965] measured the specific conductance of Red Sea water diluted to various chlorinities, at atmospheric pressure and at several temperatures. Reeburgh's results gave fair agreement with those of Thomas et al.

Park et al. [1964] and Park [1964a] show that the dissolution of calcium carbonate may result in a change of 0.006 °/oo in salinity when using conductivity measurements to estimate salinity. Park [1964b] has measured the partial equivalent conductances of 16 electrolytes in sea water.

B. PRESSURE EFFECT

One early study of the effect of pressure on conductivity was conducted by Adams and Hall [1931]. Measurements of relative resistance were made on sodium chloride solutions of various concentrations and on some other prepared solutions.

More recently, the effect of pressure on the specific conductance of sea water has been studied.

Hamon [1958] made measurements on a single sample of artificial sea water at four different temperatures. The pressure was increased in three steps by admitting compressed nitrogen to the pressure vessel to a pressure of about 900 decibars. The measurements were made adiabatically and a correction for the increase in conductance due to adiabatic heating was subtracted from the measured conductance. Hamon describes his results as tentative and estimated the accuracy of the pressure coefficients to be $\pm$ 5%. Hamon's data is presented in an inconsistent manner, however. The raw data shows resistance increasing with pressure, but the pressure coefficient of conductance is calculated as positive and in direct conflict with the data. In actuality, the latter is correct.

Horne and Frysinger [1963] measured the specific conductance of three sea water samples at four temperatures and at pressures to 13,800 decibars. The samples were made by diluting artificial sea water. Measurements were made at pressure increments of 1,380 decibars. The temperature was controlled by a constant temperature bath. After a pressure increase, conductance measurements were made until a constant result indicated the heat generated by the nearly adiabatic compression had dissipated. Horne and Frysinger found the conductivity vs. pressure plot to be linear in the range up to 6,890 decibars. Also the slope was independent of

temperature in the range 0^{o} to 25^{o} C. Horne and Frysinger concluded that in these ranges specific conductance (κ) at any pressure (P) in bars may be related to the value at atmospheric pressure by the relation:

$$\kappa_{P,T,Cl} = \kappa_{1,T,Cl} + \left[(0.35 \pm 0.25) + (0.185 \pm 0.028)\ Cl\right] 10^{-6} P$$

(The parentheses shown above were omitted in the original article, but it is obvious that the authors intended that they be included.)

Bradshaw and Schleicher [1965] determined the percentage increase in electrical conductance with pressure for real sea water of three salinities and six temperatures up to a pressure of 10,338 decibars. The pressure was increased in steps of 1,723 decibars. The temperature was observed at each data point and if there was a small deviation from the desired temperature an appropriate correction was made to the specific conductance. The precision of these measurements was estimated to be better than $\pm$ 0.01°/oo in equivalent salinity change. Bradshaw and Schleicher also developed an empirical formula for the percentage increase in conductance that fit their data with a maximum deviation of 0.005°/oo and a standard deviation of 0.002°/oo, both in equivalent salinity error. Since there are some discrepancies between the work of Horne and Frysinger and that of Bradshaw and Schleicher, further investigation is warranted.

Mays [1968] made a study of five solutions at four temperatures each up to pressures of 2,000 decibars. The solutions were real

sea water, artificial sea water, and three potassium chloride solutions. This was the first study in which the pressure was increased in relatively small increments of about 120 decibars. Measurements were made in a pressure vessel surrounded by a constant temperature copper coil, but no provision was made for measuring the temperature once the pressure was raised above atmospheric. Consequently, Mays waited 15 minutes after each pressure increase before taking measurements in order to allow the heat generated by the nearly adiabatic compression to dissipate. Mays described possible explanations for the pressure effect on specific conductance. Mays concluded that the specific conductance has a cubic or parabolic relationship to pressure. Since no temperature measurements were made, the nonlinearities observed by Mays may be due to undetected temperature fluctuations. In either event, the suggestion of a nonlinear change in specific conductance should either be refuted or verified.

III. APPARATUS

Conductance was measured with platinum electrodes inside a glass cell. The entire cell was enclosed in a stainless steel pressure vessel that had a water jacket for temperature control. Temperature, pressure and specific conductance was measured at each data point.

A. CONDUCTIVITY CELL

The conductivity cell was a glass cylinder 4-1/2 inches high and 3/4-inch inside diameter (Figure 1). Two stand-offs were located one inch below the top to keep the cell from moving within the pressure vessel. A small cover of the same material was placed over the open upper end to prevent any capacitive effect due to the stainless steel pressure vessel. The cover did not make a pressure tight seal, thus the pressure inside and outside the cell was equal at all times.

There were two openings opposite each other and one inch from the bottom to accommodate the five-inch long platinum leads for the electrodes. Outside the cell, the leads were insulated with TEFLON tape and the penetrations at the cell walls were sealed with RTV-60 Silicone Rubber Compound (TECH KITS, Demarest, N. J.).

Platinum foil electrodes, one centimeter in diameter, were tack-welded on the ends of the electrodes. The faces of the electrodes were nearly parallel and about 5/8 inch apart.

Figure 1. Glass Conductivity Cell with platinum electrodes and glass cap mounted in pressure vessel base with thermocouple.

Figure 2. Pressure Vessel disassembled to show base with conductivity cell, barrel, piston, cooling coils and bolts.

The electrodes were coated with a thin layer of platinum black. This was accomplished by filling the cell with a platinizing solution (3% platinum chloride and 0.03% lead acetate) and placing three volts D. C. across the electrodes. The voltage was maintained for 5 minutes but the polarity was reversed every 30 seconds. Then the cell was rinsed and filled with 2.0 N Sulfuric Acid; both electrodes were made negative and a piece of platinum foil with three volts positive potential was inserted through the top for a few minutes. The cell was kept full of distilled water when not in use.

B. PRESSURE VESSEL

The pressure vessel consisted of three major parts; the base, the barrel, and the piston (Figure 2). When assembled, the vessel was eight inches high, excluding the piston, and five inches in diameter; the interior cavity was seven inches deep and 1.5 inches in diameter.

The cavity extended one inch into the base and the conductivity cell was placed therein so that the platinum leads rested in the small grooves cut radially across the face of the base. The platinum leads were wrapped in TEFLON tape to provide both electrical insulation and a pressure seal. The barrel was bolted to the base by means of six bolts that passed through both pieces. A pressure seal was obtained by fitting a neoprene "O" ring (0.25-inch cross section, 2.0-inches inside diameter) in a groove on the bottom of the barrel so that it was compressed by the top of the base.

The piston was slightly smaller in diameter than the cavity. A pressure seal was obtained by fitting a neoprene "O" ring (0.156-inch cross section, 1.25-inches inside diameter) in a groove near the end of the piston. The pressure was increased by applying a force to the piston.

The base and barrel were surrounded by coils of 0.5-inch copper tubing through which a coolant was pumped. The cooling coils were covered with asbestos paper for insulation.

C. PRESSURE APPLICATION AND MEASUREMENT

The entire pressure vessel was placed in a hydraulic press and a force was applied to the piston and the base. The pressure inside the vessel was directly proportional (by a ratio dependent on the areas of the respective pistons) to the hydraulic pressure. The hydraulic pressure was measured with an 18-inch Heise pressure gauge (H35771) that had a range to 700 kg/cm^2. The gauge could be read to an accuracy of 1.0 kg/cm^2. Since the piston arrangement increased the pressure by a factor of about 1.5, this would result in an accuracy of 1.5 kg/cm^2 inside the vessel. This is an accuracy of 15 decibars which would result in a salinity error of 0.006°/oo.

D. TEMPERATURE CONTROL AND MEASUREMENT

Temperature control was achieved by pumping an ethylene glycol and water coolant through the copper tubes surrounding the pressure vessel. The coolant was kept at a constant temperature

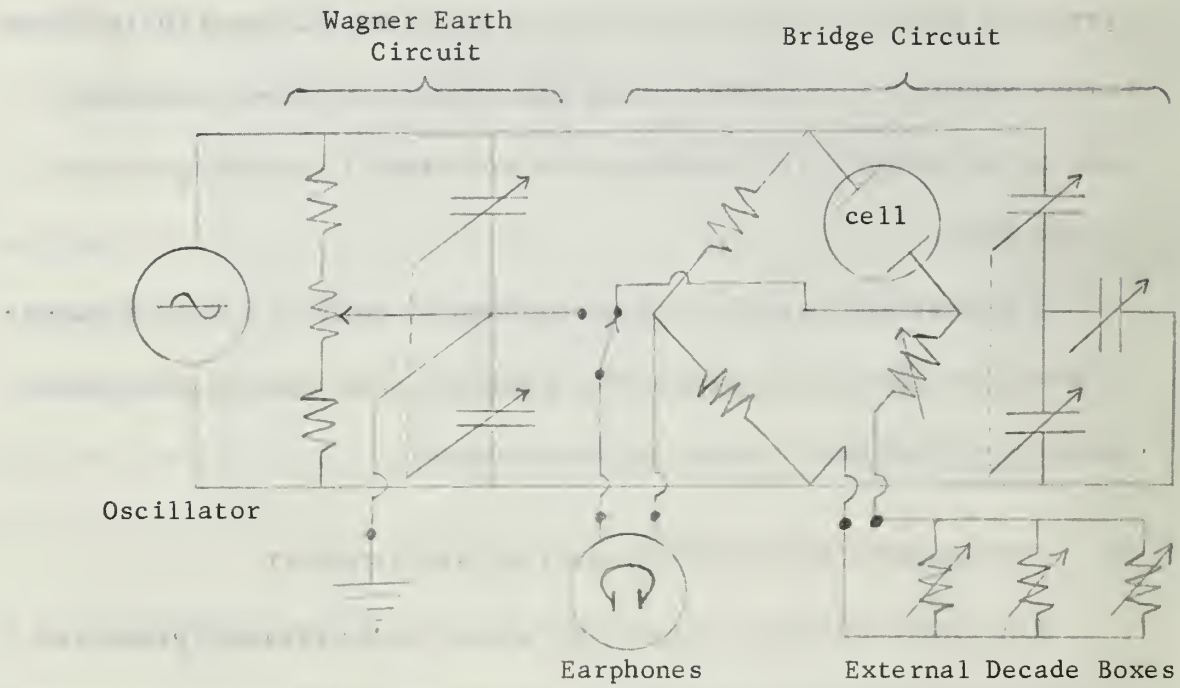

Figure 3. Simplified Schematic of Conductivity Bridge.

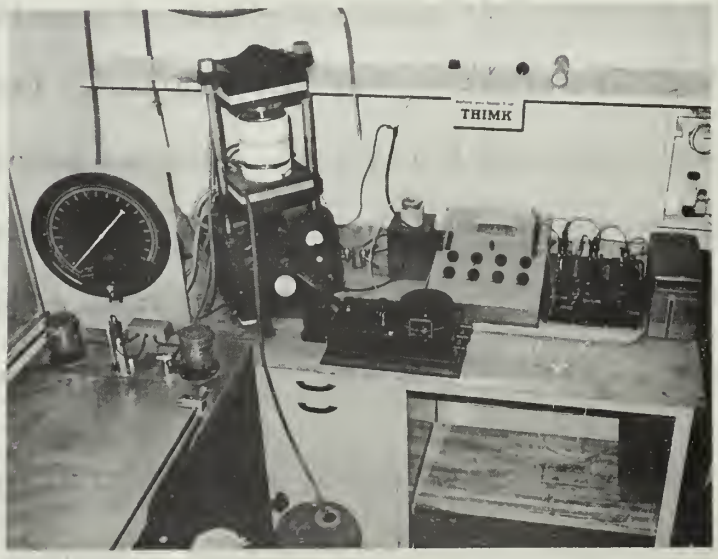

Figure 4. Apparatus; from left: temperature bath, pressure gage, hydraulic press, potentiometer, conductivity bridge, decade boxes and galvanometer.

with a 50-gallon Forma Scientific Company (Model 4-8605) temperature bath that was able to maintain a specified temperature within $\pm 0.02^{\circ}$ C.

The temperature of the sample was measured with a Copper-Constanton thermocouple located just outside the conductivity cell at the same height as the electrodes. The thermocouple leads were also insulated with TEFLON tape and led out of the pressure vessel through a radial groove in the face of the base. An ice bath was used for the exterior reference junction. The output EMF was measured with a Leeds and Northrup (Number 7552) potentiometer in conjunction with a Leeds and Northrup (Number 2430) direct current galvanometer. The precision was 0.01°C and the system was calibrated to an accuracy of 0.02°C by filling the pressure vessel with an ice-water mixture. This accuracy would result in a salinity error of $0.02^{\circ}/oo$.

E. CONDUCTIVITY MEASUREMENT

The resistivity or its inverse, the conductivity of the solution in the cell, was measured with a screened AC-fed Wheatstone bridge. The system was calibrated with a standard potassium chloride solution so that the resistivity measured could be converted to specific conductance through a cell constant.

A simplified schematic of the bridge (LKB 3216) is shown in Figure 3. It was equipped with built-in variable capacitors in order

to balance out parallel capacities in the cell or the leads. It also had a Wagner earth circuit for balancing the bridge against ground. The bridge could be operated on either 1,000 or 2,000 Hz. The internal decade resistors could be adjusted in steps of one ohm.

To attain greater accuracy three decade boxes, each accurate to 0.1 Ohm, were connected in parallel and then connected to the bridge to give an accuracy of 0.01 Ohm. Since the resistivities measured were on the order of 25 Ohms, the conductivity was measured to an accuracy of 0.000016 mho. As the cell constant was about 0.6, this would result in specific conductance accurate to 0.00001 mho/cm. This is equivalent to a salinity error of 0.01 °/oo.

The apparatus as utilized is shown in Figure 4.

F. ACCURACY AND PRECISION

The accuracy of the measurements is summarized in the following table.

	Precision	Accuracy	Equivalent Accuracy in Terms of Salinity
Pressure	1.5 kg/cm^2	1.5 kg/cm^2	0.006 °/oo
Temperature	0.01°C	0.02°C	0.02 °/oo
Specific Conductivity	0.00001 mho/cm	0.00001 mho/cm	0.01 °/oo

Thus the measurements were accurate to at least 0.036 °/oo in equivalent salinity change.

IV. EXPERIMENTAL PROCEDURE

The apparatus was calibrated at atmospheric pressure by determining a cell constant with standard potassium chloride solutions. The specific conductance of the standard solutions as well as the sea water samples was then measured at elevated pressures.

A. CELL CALIBRATION

The measurement of specific conductance would require electrodes to accurately defined area and spacing unless an effective value of length/area (ℓ /a) is determined by calibration with standard solutions. This factor (ℓ /a) is called the cell constant. It was determined by the following formula:

$$C \times \left(\frac{\ell}{a}\right) = \kappa_{True}$$

Where:

C = conductivity measured by bridge (mho)

ℓ/a = cell constant (cm^{-1})

κ_{True} = true specific conductance of standard solution from literature (mho/cm)

Once the cell constant has been determined, the specific conductance of an unknown sample can be calculated from the observed conductivity by rewriting the formula as:

$$\kappa_{OBS} = \left(\frac{\ell}{a}\right) \times C$$

Where:

C = conductivity measured by bridge (mhos)

ℓ/a = cell constant (cm^{-1})

κ_{OBS} = observed specific conductance for data point (mho/cm)

Since the electrode leads were secured by the pressure vessel and the glass cell penetrations were flexible rubber, no change in cell constant with pressure was expected.

The thermocouple was not calibrated until most of the data had been taken. The actual temperature was found to be 0.61°C below the observed temperature. A new cell constant was determined whenever any change took place (such as replacing the "0" ring between the base and barrel) that could effect the cell constant. Consequently, with the exception of the last calibration, the cell was calibrated at a temperature of 17.39°C in lieu of the 18.00°C for which accurate specific conductances have been recorded in the literature.

In order to determine the true cell constant for the earlier data, a cell constant was calculated at a true temperature of 18.00°C. This was used to calculate the specific conductance of the standard potassium chloride solutions at 17.39°C. These latter values were then used to calculate the cell constants for the earlier runs.

B. STANDARD SOLUTIONS

The most reliable values of specific conductance for potassium chloride solutions have been determined by Jones and Bradshaw [1933].

These values, along with procedures for preparing the solutions, are contained in Table I of Kortum [1965]. One N and 0.1 N solutions were prepared by weight, reduced to vacuum, according to Kortum. Baker and Adamson reagent grade (ACS code 2150) potassium chloride crystal was used. The crystal was dried by heating for several hours before weighing.

The distilled water used to make the solutions was found to have a specific conductance of 0.000014 mho/cm. This was allowed for when calculating the cell constants.

C. SEA WATER

A large volume sea water sample was obtained from a depth of three meters at a location 300 yards offshore in the southern end of Monterey Bay. This sample was divided into two parcels; the first was used as it was, while the second was allowed to evaporate slowly at room temperature until a higher salinity was attained.

The salinity of both parcels was determined by repeated measurements on an Industrial Instruments Inductive Salinometer (model RS-7B). The salinities were 32.448 and 37.152 °/oo.

For each of the two salinities, pressure runs were planned for six temperatures from 3°C to 18°C at 3°C intervals. For comparison, pressure runs were planned for the two standard solutions at 18°C only. Due to the error in the thermocouple, the runs were actually made at temperatures 0.61°C below these values.

D. MEASUREMENTS

Both the conductivity cell and the pressure vessel were filled with the solution to be studied. Before filling, however, the equipment was rinsed twice with distilled water and then twice with portions of the solution to be used. Any particular aliquot was never reused.

After filling the cell and vessel, the glass cap and piston were installed. After an observation at atmospheric pressure, observations were made at pressure increments of about 280 decibars to a pressure of 4,000 decibars. The pressure was then reduced in increments such that observations were made at pressures about midway between those observed when the pressure was increased. Thus, the pressure spacing between adjacent data points was about 140 decibars.

The temperature bath had been adjusted to give the desired temperature within the vessel; however, the pressure increases or decreases resulted in adiabatic heating or cooling of the sample solution. After a pressure change, the bridge was balanced and the temperature was measured alternately until the temperature stabilized (observed temperature within 0.03°C of desired temperature); then the pressure, temperature and bridge resistances were recorded. During data reduction, a correction was made for the occasional small differences (less than 0.03°C) between the observed and desired temperatures. Adjustments to the coolant temperature were

necessary when reversing the direction of pressure change caused adiabatic cooling in lieu of adiabatic heating or when the ambient temperature changed.

Measurements were normally made at a frequency of 2, 000 Hz; however, occasionally a valve was checked at 1, 000 Hz to insure the observations were independent of frequency.

V. DATA REDUCTION

The raw data, consisting of uncorrected temperature, hydraulic press pressure, and the resistivity of the bridge and three external decade boxes, was punched onto IBM cards and processed on an IBM 360 computer at the Naval Postgraduate School.

A. TEMPERATURE

A correction of 0.61°C (determined by the thermocouple calibration) was subtracted from each temperature.

B. PRESSURE

The sample pressure inside the vessel was related to the oil pressure in the hydraulic press by the equation:

$$P_w \times \frac{\pi}{4} D_w^2 = \text{Force} = P_h \times \frac{\pi}{4} D_h^2$$

Where:

P_w = unknown sample pressure in vessel $\left(kg/cm^2\right)$

D_w = diameter of vessel piston = 1.530 inches

D_h = diameter of hydraulic piston = 1.875 inches

P_h = observed hydraulic pressure $\left(kg/cm^2\right)$

The above may be rewritten:

$$P_w = P_h \times \left(\frac{D_h}{D_w}\right)^2$$

After the sample pressure inside the vessel was obtained in kilograms per square centimeter, it was converted to decibars using the following factors:

$$P\ \left(\text{newtons/m}^2\right) = 98066.5 \times P\ \left(\text{kg/cm}^2\right)$$

$$P\ \left(\text{decibars}\right) = 10^{-4} \times P\left(\text{newtons/m}^2\right)$$

C. SPECIFIC CONDUCTANCE

Three external decade boxes were connected in parallel. This external resistivity was then connected in series with the internal resistivity of the conductivity bridge (LKB 3216).

The external resistivity (R_e) in ohms was calculated from the resistivity of the decade boxes (R_1, R_2 and R_3) by the following formula:

$$R_e = \frac{R_1 \times R_2 \times R_3}{(R_1 \times R_2) + (R_2 \times R_3) + (R_3 \times R_1)}$$

The external resistivity and a calibration constant (R_c) of 0.06 ohm were added to the resistivity measured by the conductivity bridge (R_{cb}) to obtain the total resistivity (R_t) in ohms:

$$R_t = R_{cb} + R_c + R_e$$

The observed conductivity (C) in mhos is the reciprocal of the total resistivity (R_t):

$$C = \frac{1}{R_t}$$

This may be substituted in the equation for the specific conductance of an unknown sample, $\kappa_{OBS} = \left(\frac{\ell}{a}\right) \times C$, to obtain the specific conductance in mhos per centimeter in terms of the cell constant (ℓ /a) and the total resistivity:

$$\kappa_{OBS} = \left(\frac{\ell}{a}\right) \times \frac{1}{R_t}$$

In those cases where the observed temperature was not exactly equal to the desired run temperature, a small but significant correction was applied to the specific conductance. The temperature coefficient of specific conductance at atmospheric pressure was used [Weyl, 1964].

VI. RESULTS

The results for sea water of salinity 32.448 °/oo are in Table I. The results for sea water of salinity 37.152 °/oo are in Table II. The results for the potassium chloride solutions are in Table III.

The increase of specific conductance with pressure in the range studied is nearly linear. There is, however, a small but significant departure from linearity. When least square curves of various degrees were fit to the data, it was found that linear curves had an average standard deviation of 0.058 °/oo in salinity equivalent while the second and third degree curves both had an average standard deviation of 0.041 °/oo in salinity equivalent.

The measurements were considered to have an accuracy of better than 0.036 °/oo; the standard deviation of both the second and third degree curves approach this accuracy while the standard deviation of the linear curves is significantly higher.

Plots of the data from two typical pressure runs with first, second and third degree curves fit to the data are shown in Figures 5 and 6. Note the concave downward curvature of the data. Thus, in the range studied, the change in specific conductance with pressure should be described by a second degree, or higher, polynomial if high accuracy is desired.

For example, at a salinity of 37.152 °/oo, a temperature of 17.39°C, and a pressure of 2,000 decibars, the specific conductance

TEMPERATURE 17.39 DEG C		TEMPERATURE 14.39 DEG C		TEMPERATURE 11.39 DEG C	
PRESSURE DECIBARS	SP. CONDUCTANCE MHOS/CM	PRESSURE DECIBARS	SP. CONDUCTANCE MHOS/CM	PRESSURE DECIBARS	SP. CONDUCTANCE MHOS/CM
0.0	0.04164	0.0	0.03909	0.0	0.03648
309.3	0.04179	304.9	0.03916	262.2	0.03659
574.4	0.04190	589.1	0.03932	618.6	0.03674
876.3	0.04204	898.4	0.03945	905.8	0.03682
1193.0	0.04215	1178.2	0.03958	1190.0	0.03693
1487.5	0.04228	1512.5	0.03971	1502.2	0.03708
1782.1	0.04239	1811.5	0.03983	1774.7	0.03720
2081.0	0.04251	2061.9	0.03988	2047.2	0.03730
2356.5	0.04261	2400.6	0.04001	2385.9	0.03744
2673.1	0.04272	2665.7	0.04011	2661.3	0.03755
2967.7	0.04284	2945.6	0.04020	2952.9	0.03762
3284.3	0.04293	3254.9	0.04031	3254.9	0.03772
3520.0	0.04302	3559.7	0.04040	3490.5	0.03780
3844.0	0.04310	3826.3	0.04052	3755.6	0.03785
4168.0	0.04320	3947.1	0.04049	4094.3	0.03799
3969.2	0.04299	3684.9	0.04031	3858.7	0.03790
3718.8	0.04296	3424.2	0.04025	3752.7	0.03775
3449.3	0.04293	3117.9	0.04022	3394.8	0.03765
3100.2	0.04281	2820.4	0.04013	3137.0	0.03754
2835.1	0.04275	2533.2	0.04009	2798.3	0.03749
2518.5	0.04272	2206.2	0.03999	2547.9	0.03745
2195.9	0.04260	1914.6	0.03990	2234.2	0.03739
1948.5	0.04251	1612.7	0.03977	1936.7	0.03726
1642.2	0.04235	1310.8	0.03962	1634.8	0.03714
1303.4	0.04236	1016.2	0.03947	1355.0	0.03703
1045.7	0.04225	721.7	0.03932	1060.4	0.03690
751.1	0.04207	456.6	0.03922	758.5	0.03679
434.5	0.04190	147.3	0.03906	456.6	0.03666
132.5	0.04173	0.0	0.03900	139.9	0.03650
0.0	0.04167			0.0	0.03644

Table I. Experimental Results for Sea Water of Salinity 32.448 °/oo.

TEMPERATURE 8.39 DEG C		TEMPERATURE 5.39 DEG C		TEMPERATURE 2.39 DEG C	
PRESSURE DECIBARS	SP. CONDUCTANCE MHOS/CM	PRESSURE DECIBARS	SP. CONDUCTANCE MHOS/CM	PRESSURE DECIBARS	SP. CONDUCTANCE MHOS/CM
0.0	0.03404	0.0	0.03129	0.0	0.02884
309.3	0.03417	294.6	0.03141	287.2	0.02893
611.2	0.03431	618.6	0.03156	552.3	0.02908
894.0	0.03444	889.6	0.03167	913.1	0.02922
1222.4	0.03457	1148.8	0.03176	1207.7	0.02935
1458.1	0.03468	1458.1	0.03191	1487.5	0.02946
1737.9	0.03466	1789.4	0.03204	1760.0	0.02957
2061.9	0.03480	2079.6	0.03215	2091.4	0.02970
2327.0	0.03489	2356.5	0.03223	2390.3	0.02983
2592.1	0.03500	2680.5	0.03235	2665.7	0.02993
2950.0	0.03512	2919.1	0.03237	2966.2	0.03003
3218.0	0.03522	3240.1	0.03251	3218.0	0.03012
3520.0	0.03532	3542.1	0.03261	3549.4	0.03018
3829.2	0.03542	3799.8	0.03271	3832.2	0.03029
4123.8	0.03549	3947.1	0.03275	4057.5	0.03038
3961.8	0.03540	3754.1	0.03266	3674.6	0.03029
3652.5	0.03523	3446.3	0.03259	3402.1	0.03014
3406.6	0.03516	3107.6	0.03252	3122.3	0.03008
3128.2	0.03512	2827.7	0.03247	2857.2	0.03003
2842.5	0.03508	2525.8	0.03234	2496.4	0.02991
2581.8	0.03500	2231.3	0.03223	2231.3	0.02971
2241.6	0.03487	1929.3	0.03210	1885.2	0.02963
1936.7	0.03476	1649.5	0.03198	1679.0	0.02962
1649.5	0.03459	1332.9	0.03184	1360.7	0.02956
1355.0	0.03446	1075.1	0.03191	1063.3	0.02940
1038.3	0.03443	721.7	0.03162	721.7	0.02924
758.5	0.03435	471.3	0.03152	463.9	0.02911
456.6	0.03416	150.2	0.03133	147.3	0.02893
154.6	0.03400	0.0	0.03125	0.0	0.02886

Table I (con't.) Experimental Results for Sea Water of Salinity 32.448 °/oo.

TEMPERATURE 17.39 DEG C		TEMPERATURE 14.39 DEG C		TEMPERATURE 11.39 DEG C	
PRESSURE DECIBARS	SP. CONDUCTANCE MHOS/CM	PRESSURE DECIBARS	SP. CONDUCTANCE MHOS/CM	PRESSURE DECIBARS	SP. CONDUCTANCE MHOS/CM
0.0	0.04695	0.0	0.04407	0.0	0.04111
279.8	0.04705	301.9	0.04421	294.6	0.04122
596.5	0.04720	589.1	0.04432	596.5	0.04136
883.7	0.04735	913.1	0.04449	883.7	0.04155
1200.3	0.04749	1185.6	0.04460	1222.4	0.04166
1480.1	0.04764	1494.9	0.04475	1505.2	0.04178
1774.7	0.04774	1767.3	0.04489	1796.8	0.04193
2076.6	0.04785	2076.6	0.04504	2076.6	0.04203
2349.1	0.04800	2341.7	0.04512	2327.0	0.04213
2628.9	0.04809	2695.2	0.04527	2702.6	0.04229
2952.9	0.04821	2930.8	0.04539	2975.0	0.04242
3195.9	0.04831	3254.9	0.04550	3225.4	0.04250
3542.1	0.04845	3549.4	0.04562	3195.9	0.04243
3836.6	0.04855	3755.6	0.04567	3549.4	0.04260
4064.9	0.04860	4123.8	0.04574	3821.9	0.04270
3976.5	0.04846	3939.7	0.04559	4168.0	0.04283
3637.8	0.04833	3696.7	0.04555	3961.8	0.04265
3409.5	0.04830	3424.2	0.04548	3652.5	0.04248
3122.3	0.04826	3144.4	0.04543	3387.4	0.04244
2857.2	0.04820	2835.1	0.04531	3092.8	0.04236
2511.1	0.04806	2518.5	0.04520	2849.8	0.04233
2238.6	0.04795	2246.0	0.04506	2540.6	0.04223
1907.3	0.04780	1936.7	0.04492	2238.6	0.04208
1634.8	0.04771	1642.2	0.04478	1936.7	0.04195
1347.6	0.04758	1355.0	0.04463	1656.9	0.04181
1053.0	0.04743	1045.7	0.04449	1340.2	0.04164
751.1	0.04732	751.1	0.04429	1045.7	0.04156
456.6	0.04716	456.6	0.04421	751.1	0.04142
154.6	0.04698	147.3	0.04405	441.8	0.04125
				132.5	0.04107

Table II. Experimental Results for Sea Water of Salinity 37.152 °/oo.

TEMPERATURE 8.39 DEG C		TEMPERATURE 5.39 DEG C		TEMPERATURE 2.39 DEG C	
PRESSURE DECIBARS	SP. CONDUCTANCE MHOS/CM	PRESSURE DECIBARS	SP. CONDUCTANCE MHOS/CM	PRESSURE DECIBARS	SP. CONDUCTANCE MHOS/CM
0.0	0.03832	0.0	0.03531	0.0	0.03255
324.0	0.03842	312.2	0.03544	279.8	0.03267
611.2	0.03857	603.8	0.03558	633.3	0.03283
905.8	0.03871	888.1	0.03573	898.4	0.03297
1215.0	0.03884	1193.0	0.03587	1215.0	0.03312
1494.9	0.03899	1472.8	0.03598	1483.1	0.03324
1782.1	0.03912	1752.6	0.03615	1789.4	0.03339
2054.5	0.03923	2061.9	0.03628	2076.6	0.03353
2356.5	0.03935	2327.0	0.03633	2366.8	0.03366
2665.7	0.03950	2651.0	0.03650	2643.6	0.03377
2930.8	0.03961	2952.9	0.03665	2930.8	0.03389
3254.9	0.03969	3225.4	0.03676	3284.3	0.03403
3520.0	0.03981	3534.7	0.03687	3564.1	0.03412
3829.2	0.03991	3829.2	0.03695	3844.0	0.03421
4050.2	0.03999	4123.8	0.03705	4109.1	0.03430
3927.9	0.03983	3976.5	0.03693	3947.1	0.03422
3655.5	0.03973	3652.5	0.03683	3696.7	0.03416
3358.0	0.03965	3402.1	0.03680	3372.7	0.03400
3144.4	0.03959	3122.3	0.03676	3114.9	0.03399
2776.2	0.03950	2842.5	0.03666	2832.2	0.03394
2525.8	0.03947	2496.4	0.03645	2555.3	0.03384
2223.9	0.03932	2253.4	0.03641	2238.6	0.03372
1929.3	0.03921	1944.1	0.03628	1936.7	0.03359
1639.2	0.03903	1649.5	0.03613	1664.2	0.03339
1347.6	0.03886	1369.7	0.03598	1325.5	0.03322
1053.0	0.03876	1045.7	0.03581	1053.0	0.03309
721.7	0.03852	717.3	0.03566	684.8	0.03291
441.8	0.03843	441.8	0.03555	456.6	0.03278
147.3	0.03824	137.0	0.03533	154.6	0.03257

Table II (con't.) Experimental Results for Sea Water of Salinity 37.152 °/oo.

KCL 1.0 N		KCL 0.1 N	
TEMPERATURE 17.39 DEG C		TEMPERATURE 17.39 DEG C	
PRESSURE DECIBARS	SP. CONDUCTANCE MHOS/CM	PRESSURE DECIBARS	SP. CONDUCTANCE MHOS/CM
0.0	0.09678	0.0	0.01111
301.9	0.09724	265.1	0.01114
574.4	0.09744	584.7	0.01117
817.4	0.09763	839.5	0.01121
1178.2	0.09790	1178.2	0.01125
1480.1	0.09824	1458.1	0.01129
1789.4	0.09844	1737.9	0.01132
2091.4	0.09857	2076.6	0.01134
2378.5	0.09877	2356.5	0.01137
2665.7	0.09898	2695.2	0.01142
2930.8	0.09905	2920.5	0.01143
3259.3	0.09918	3240.1	0.01147
3530.3	0.09939	3527.3	0.01150
3866.1	0.09966	3792.4	0.01151
4109.1	0.09987	4087.0	0.01153
4359.4	0.10015	3986.8	0.01152
4654.0	0.10029	3733.5	0.01151
4955.9	0.10041	3446.3	0.01150
4852.8	0.10001	3122.3	0.01147
4587.7	0.10001	2790.9	0.01145
4212.2	0.09987	2547.9	0.01142
3983.9	0.09961	2253.4	0.01138
3704.1	0.09961	1944.1	0.01134
3424.2	0.09946	1649.5	0.01131
3092.8	0.09918	1303.4	0.01129
2798.3	0.09898	1060.4	0.01125
2459.6	0.09884	743.8	0.01121
2246.0	0.09866	456.6	0.01117
1929.3	0.09834	147.3	0.01112
1664.2	0.09814		
1296.0	0.09793		
1060.4	0.09770		
765.8	0.09728		
456.6	0.09696		
147.3	0.09665		

Table III. Experimental Results for Potassium Chloride Solutions.

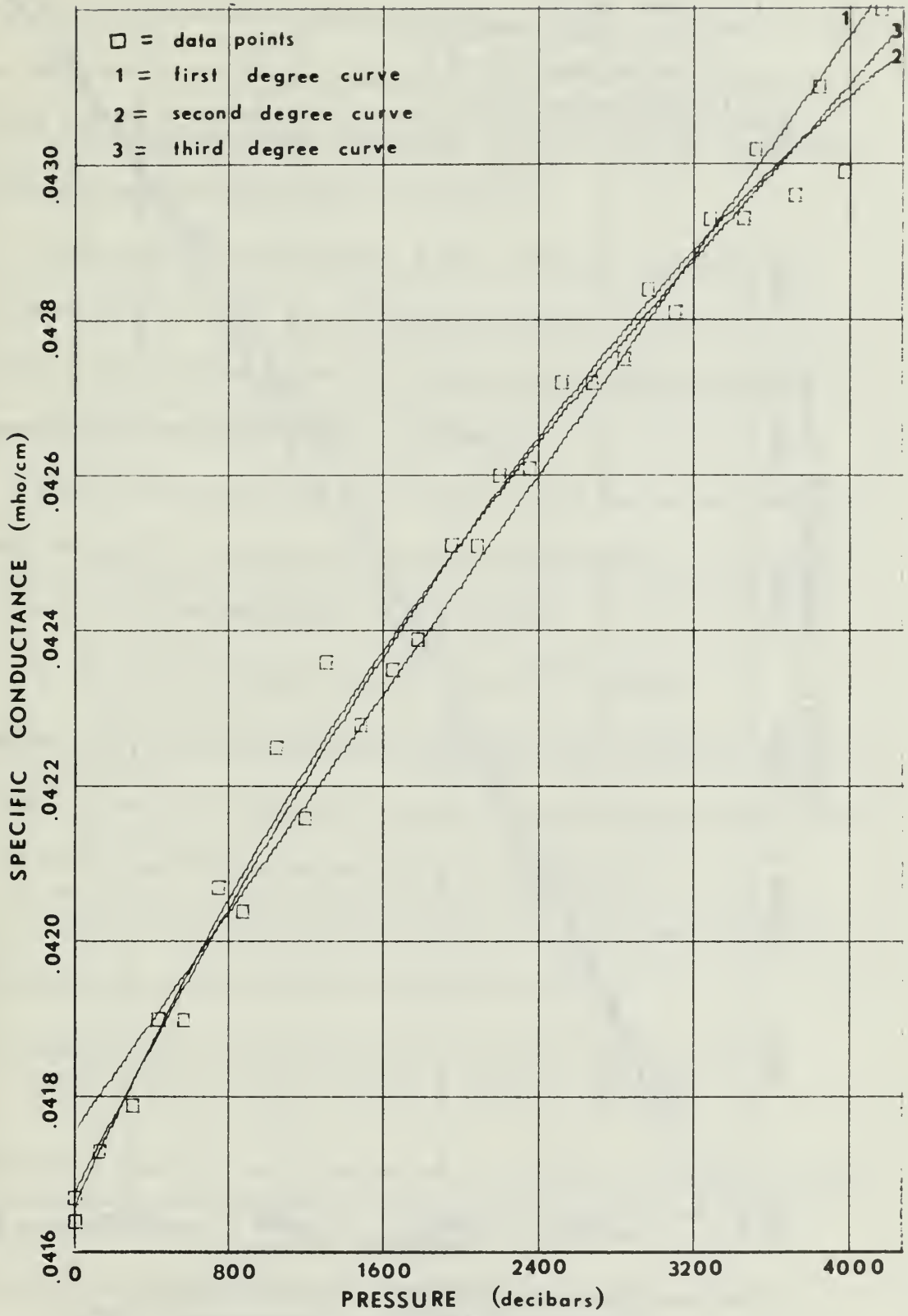

Figure 5. Specific Conductance vs. Pressure, Salinity 32.448 °/oo, Temperature 17.39°C.

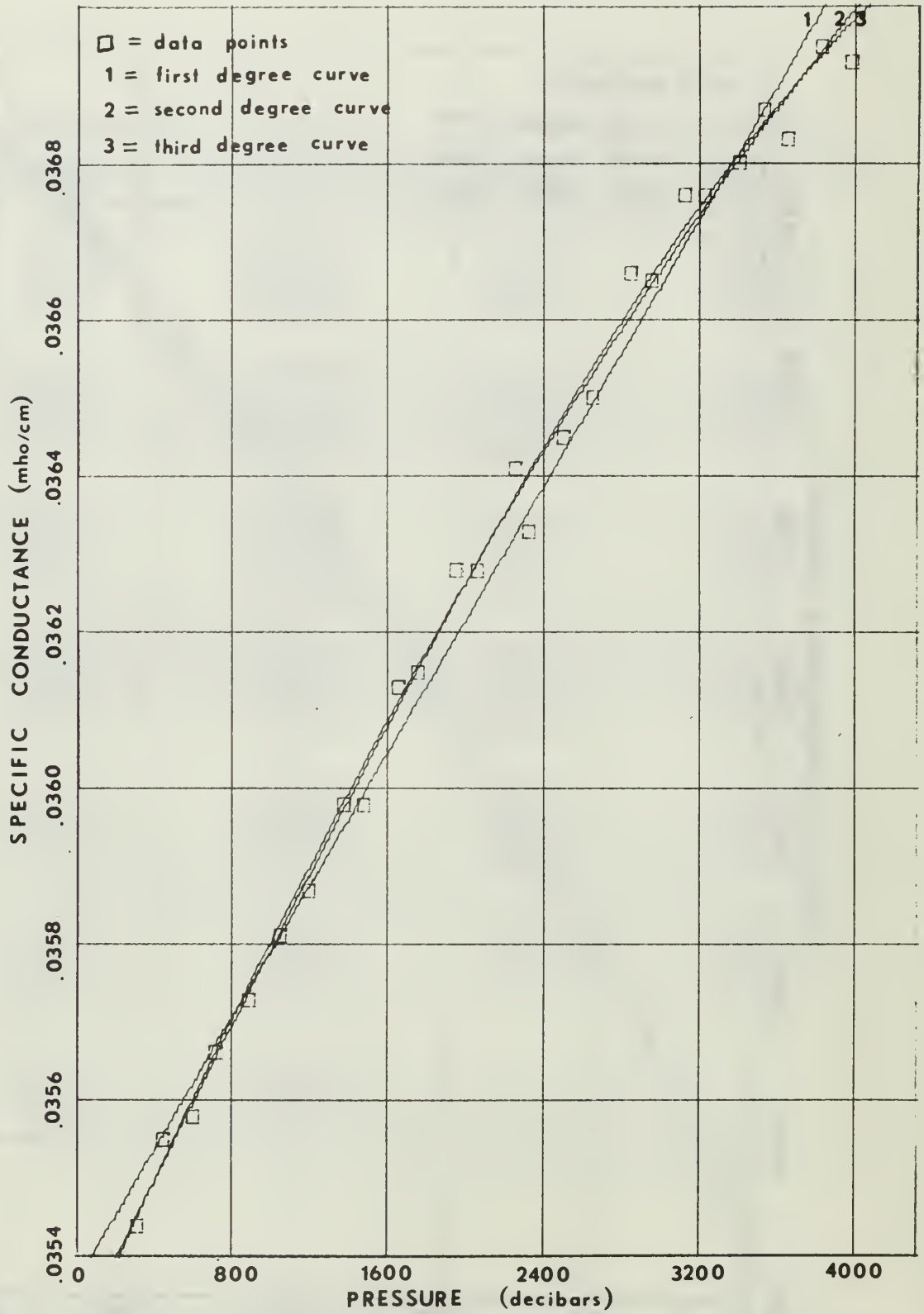

Figure 6. Specific Conductance vs. Pressure, Salinity 37.152 °/oo, Temperature 5.39°C.

calculated from a first degree polynomial will be in error by 0.047 °/oo in salinity equivalent when compared with the value calculated by a third degree polynomial. This error is larger than the maximum possible experimental error of 0.036 °/oo.

Since the best experimental work in the past (Bradshaw and Schleicher) has used a third degree polynomial to describe the results, a third degree in lieu of a second degree polynomial will be used to describe the results of this study.

The coefficients of the least square, third degree polynomials describing the behavior of the specific conductance (K) are shown in Table IV. The polynomial is of the form:

$$K(S_1, T_1, P) = A(1) + A(2)xP + A(3)xP^2 + A(4)xP^3$$

where A(i) are the coefficients and the pressure (P) is in decibars. These curves fit the data with a standard deviation that is less than 0.05 °/oo in equivalent salinity error in all cases.

The coefficients of the least square, third degree polynomials describing the behavior of the conductivity ratio

$$\frac{C(S_1, T_1, P)}{C(S_1, T_1, 0)} = B(1) + B(2)xP + B(3)xP^2 + B(4)xP^3$$

where B(i) are the coefficients and the pressure (P) is in decibars are shown in Table V. These curves fit the data with a standard deviation of about 0.05 °/oo in equivalent salinity error.

TABLE IV. Coefficients of the Polynomial: $\mathcal{K}(S_1,T_1,P) = A(1) + A(2)xP + A(3)xP^2 + A(4)xP^3$

Salinity(S_1)	Temp(T_1)	A(1)	A(2)	A(3)	A(4)
32.448	17.39	0.41653×10^{-1}	0.55369×10^{-6}	-0.76614×10^{-10}	0.71320×10^{-14}
32.448	14.39	0.39013×10^{-1}	0.53393×10^{-6}	-0.56342×10^{-10}	0.37242×10^{-14}
32.448	11.39	0.36446×10^{-1}	0.49153×10^{-6}	-0.49826×10^{-10}	0.47539×10^{-14}
32.448	8.39	0.34004×10^{-1}	0.46831×10^{-6}	-0.49789×10^{-10}	0.54241×10^{-14}
32.448	5.39	0.31270×10^{-1}	0.49479×10^{-6}	-0.37116×10^{-10}	0.14625×10^{-14}
32.448	2.39	0.28845×10^{-1}	0.52453×10^{-6}	-0.65155×10^{-10}	0.69705×10^{-14}
37.152	17.39	0.46922×10^{-1}	0.51342×10^{-6}	-0.23042×10^{-10}	-0.12013×10^{-14}
37.152	14.39	0.44038×10^{-1}	0.40628×10^{-6}	0.57599×10^{-10}	-0.14275×10^{-13}
37.152	11.39	0.41056×10^{-1}	0.52009×10^{-6}	-0.28404×10^{-10}	0.45578×10^{-15}
37.152	8.39	0.38237×10^{-1}	0.50389×10^{-6}	0.47851×10^{-12}	-0.56015×10^{-14}
37.152	5.39	0.35293×10^{-1}	0.49740×10^{-6}	0.55362×10^{-11}	-0.60947×10^{-14}
37.152	2.39	0.32520×10^{-1}	0.52977×10^{-6}	0.15024×10^{-11}	-0.66014×10^{-14}
1.0 N KCl	17.39	0.96687×10^{-1}	0.11367×10^{-5}	-0.14691×10^{-9}	0.13317×10^{-13}
0.1 N KCl	17.39	0.11107×10^{-1}	0.12661×10^{-6}	0.46809×10^{-12}	-0.14853×10^{-14}

TABLE V. Coefficients of the Polynomial:

$$\frac{C(S_1,T_1,P)}{C(S_1,T_1,0)} = B(1) + B(2)xP + B(3)xP^2 + B(4)xP^3$$

Salinity(S_1)	Temp(T_1)	B(1)	B(2)	B(3)	B(4)
32.448	17.39	1.00000	0.13825×10^{-4}	-0.20894×10^{-8}	0.20572×10^{-12}
32.448	14.39	0.99999	0.10026×10^{-4}	0.36129×10^{-9}	-0.16562×10^{-12}
32.448	11.39	0.99999	0.11834×10^{-4}	-0.57919×10^{-9}	0.19883×10^{-13}
32.448	8.39	0.99999	0.11912×10^{-4}	-0.58595×10^{-9}	0.37570×10^{-13}
32.448	5.39	0.99999	0.14633×10^{-4}	-0.60183×10^{-9}	-0.37707×10^{-13}
32.448	2.39	1.00000	0.18495×10^{-4}	-0.24085×10^{-8}	0.26288×10^{-12}
37.152	17.39	0.99999	0.98826×10^{-5}	0.14239×10^{-10}	-0.96324×10^{-13}
37.152	14.39	0.99999	0.79300×10^{-5}	0.19220×10^{-8}	-0.40970×10^{-12}
37.152	11.39	0.99999	0.10373×10^{-4}	0.37620×10^{-9}	-0.13552×10^{-12}
37.152	8.39	0.99999	0.92584×10^{-5}	0.18898×10^{-8}	-0.41070×10^{-12}
37.152	5.39	0.99999	0.13214×10^{-4}	0.57177×10^{-9}	-0.23027×10^{-12}
37.152	2.39	0.99999	0.14644×10^{-4}	0.82603×10^{-9}	-0.31163×10^{-12}

VII. COMPARISON WITH PREVIOUS INVESTIGATIONS

A. ATMOSPHERIC PRESSURE

The observed values of specific conductance at atmospheric pressure were found to be 0.5% to 1.0% below the values reported by Thomas et al. [1934] or Reeburgh [1965]. Thomas et al. and Reeburgh differ from each other by about 0.2%. The reason for this small disagreement with the earlier values at atmospheric pressure is unknown.

B. ELEVATED PRESSURES

1. Hamon

Hamon [1958] reports linear pressure coefficients of the conductivity ratio for sea water of salinity 35.6 °/oo (Cl = 19.7 °/oo) at four temperatures. The values at 11.0°C and 6.6°C may be compared with most of the later investigators. The pressure range under consideration is 0 to 1,000 decibars. For each investigation, the mean pressure coefficient or the linear pressure coefficient is reported in Table VI. Note that the best consistant agreement is between Bradshaw and Schleicher [1965] and this report.

Hamon made his measurements under nearly adiabatic conditions and then applied a correction for the conductivity increase due to adiabatic heating. As Bradshaw and Schleicher [1965] have previously suggested, a significant amount of heat was probably

TABLE VI. Linear Pressure Coefficients of Conductivity Ratio (x 10^{-5} decibars^{-1}) for sea water of 35.6 °/oo and 0 to 1,000 decibars.

Temp	Hamon	Horne & Frysinger	Bradshaw & Schleicher	This Report
11.0	1.00	1.01	1.13	1.19
6.6	1.16	0.97	1.28	1.33

TABLE VII. Linear Pressure Coefficients of Specific Conductance (x 10^{-7} decibar $^{-1}$) for sea water at 0 to 4,000 decibars.

Investigator	Temp °C	Salinity 32.448 °/oo	Salinity 37.152 °/oo
H & F max	0 to 25	4.426	4.980
H & F mean	0 to 25	3.673	4.155
H & F min	0 to 25	2.920	3.329
This Report	2.39	3.692	4.339
This Report	5.39	3.713	4.259
This Report	8.39	3.634	4.205
This Report	11.39	3.630	4.101
This Report	14.39	3.676	4.235
This Report	17.39	3.523	4.003

lost and this caused Hamon's values to be 14% lower than the results of this investigation.

Further comparison with Hamon's data is impossible since it has been presented erroneously. Hamon's data shows increasing resistance for both increasing temperature and increasing pressure. The reverse is, of course, true in both cases.

2. Horne and Frysinger

Horne and Frysinger [1963] concluded that the effect of pressure is linear and independent of temperature in the range 0^{o} to 25^{o}C and up to 6,890 decibars.

As has been previously shown, the effect cannot be accurately described as linear even at these relatively low pressures.

However, for comparison, values of the linear pressure coefficient were calculated for the salinities used in this study (Cl = 17.961 $^{o}/_{oo}$ and Cl = 37.152 $^{o}/_{oo}$) from Horne and Frysinger's formula:

$$K_{P,T,Cl} = K_{1,T,Cl} + \left[(0.35 \pm 0.25) + (0.185 \pm 0.028)\,Cl\right] 10^{-6} P$$

where pressure (P) is in bars. A mean value as well as maximum and minimum values were calculated. These are compared with the results of this study in Table VII.

It can be seen that all of the present values fall within the rather large deviation described by Horne and Frysinger.

A definite trend with temperature is also discernable. In general, at lower temperatures the effect of pressure is greater

than at higher temperatures. This is exactly what one would expect since, in the pressure range studied, the change in viscosity with pressure is small above 10°C while the viscosity decreases rapidly with pressure at temperatures below 10°C [Horne and Johnson, 1966b]. The decreased viscosity indicates greater molecular mobility which leads to increased conductance. All investigations shown in Table VI, except Horne and Frysinger, show this temperature trend.

The use of Horne and Frysinger's first degree polynomial at 2,000 decibars will result in the following equivalent salinity errors when compared with a third degree polynomial derived from the results of this study.

Temp	Salinity 32.448 °/oo	Salinity 37.152 °/oo
5.39°C	0.14 °/oo	0.15°/oo
11.39°C	0.09 °/oo	0.09°/oo

These large differences result from Horne and Frysinger's linear approximation of a higher order effect and from the temperature effect on the pressure coefficients of conductivity.

3. Bradshaw and Schleicher

Bradshaw and Schleicher [1965] gave their results in the form of a polynomial for $\frac{C(S_1, T_1, P)}{C(S_1, T_1, 0)}$ which is first degree in salinity and third degree in temperature and pressure. The present data was compared with this polynomial and the agreement was found to be good. The agreement of the linear coefficients shown in Table VI is also good.

The data from this investigation fit Bradshaw and Schelicher's equation with a standard deviation of 0.066 °/oo in salinity equivalent.

The conductivity ratios calculated from the present data have been plotted with lines of corresponding conductivity ratios calculated from Bradshaw and Schleicher's equation; these are shown in Figures 7 and 8.

Nearly 500 pairs of conductivity ratios, one calculated from Table V and the other calculated from Bradshaw and Schleicher's equation, were compared. The resulting standard deviation was 0.05 °/oo in equivalent salinity. This is a significant error, but the standard deviation of the data from the third degree curves fit to the data is also on the order of 0.05 °/oo in equivalent salinity. Thus Bradshaw and Schleicher's equation fits the present data nearly as well as a third degree equation can. Because of this and because Bradshaw and Schleicher's equation was derived for a wider range of pressures and salinities than was studied in this work, no modifications to the equation are proposed.

4. Mays

Mays [1968] found significant nonlinearities in the relation between specific conductance and pressure. Mays was unable to conclude which degree polynomial should be used to describe the effect and none was reported. Thus quantitative comparison is impossible.

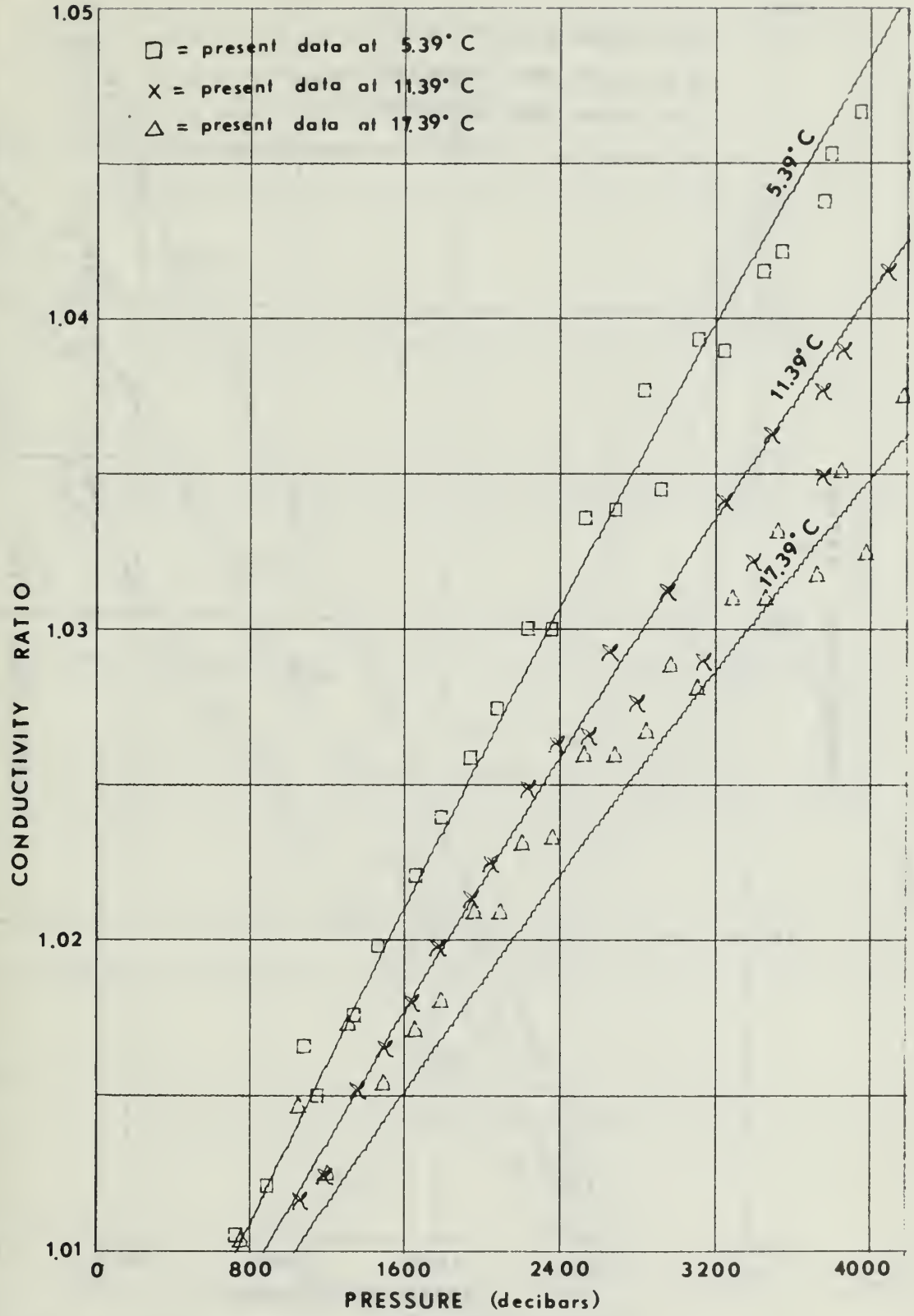

Figure 7a. Conductivity Ratio Vs. Pressure, Salinity 32.448 °/oo; Points - Present Data; Lines - Bradshaw & Schleicher.

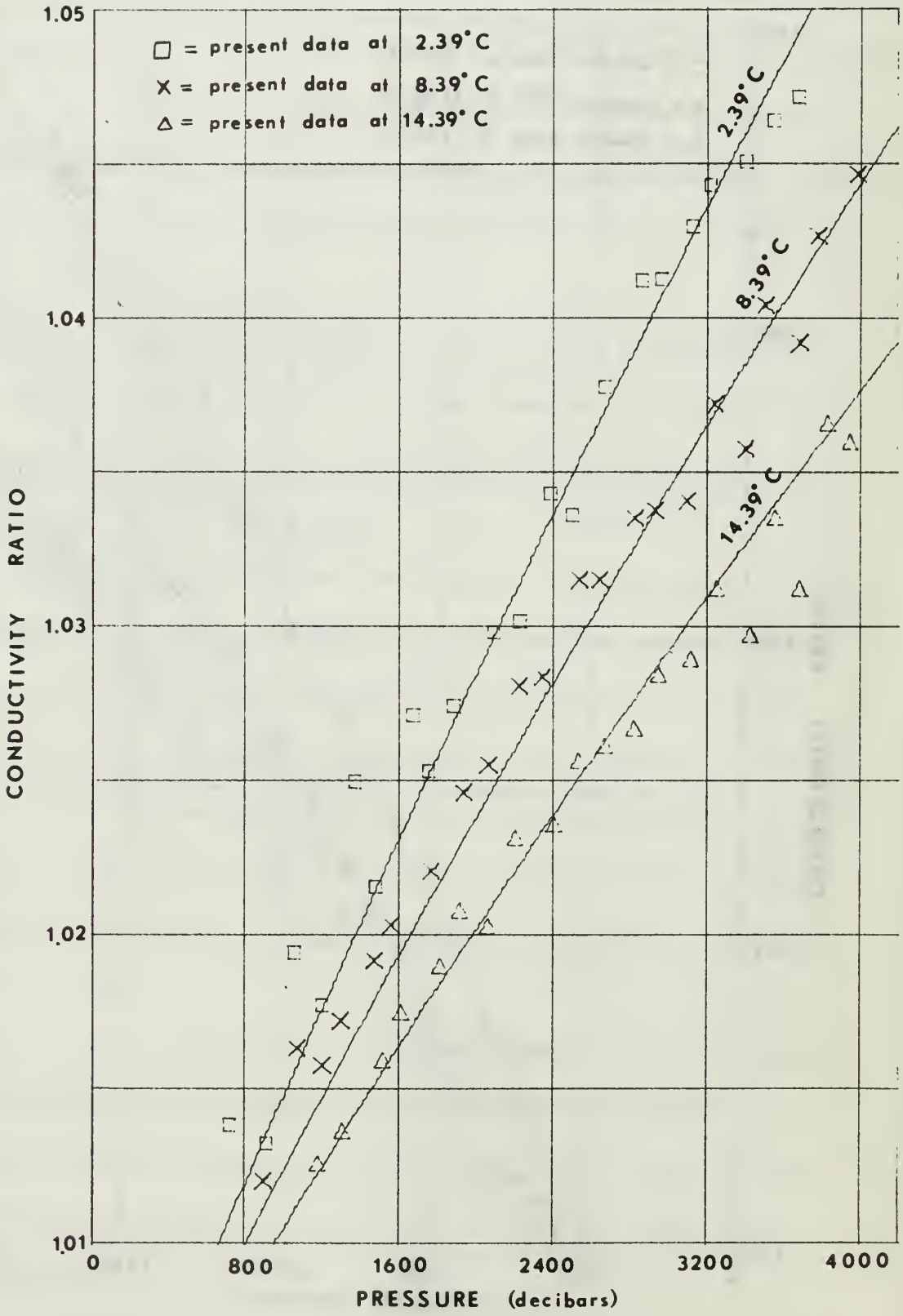

Figure 7b. Conductivity Ratio Vs. Pressure, Salinity 32.448 °/oo; Points - Present Data; Lines - Bradshaw & Schleicher.

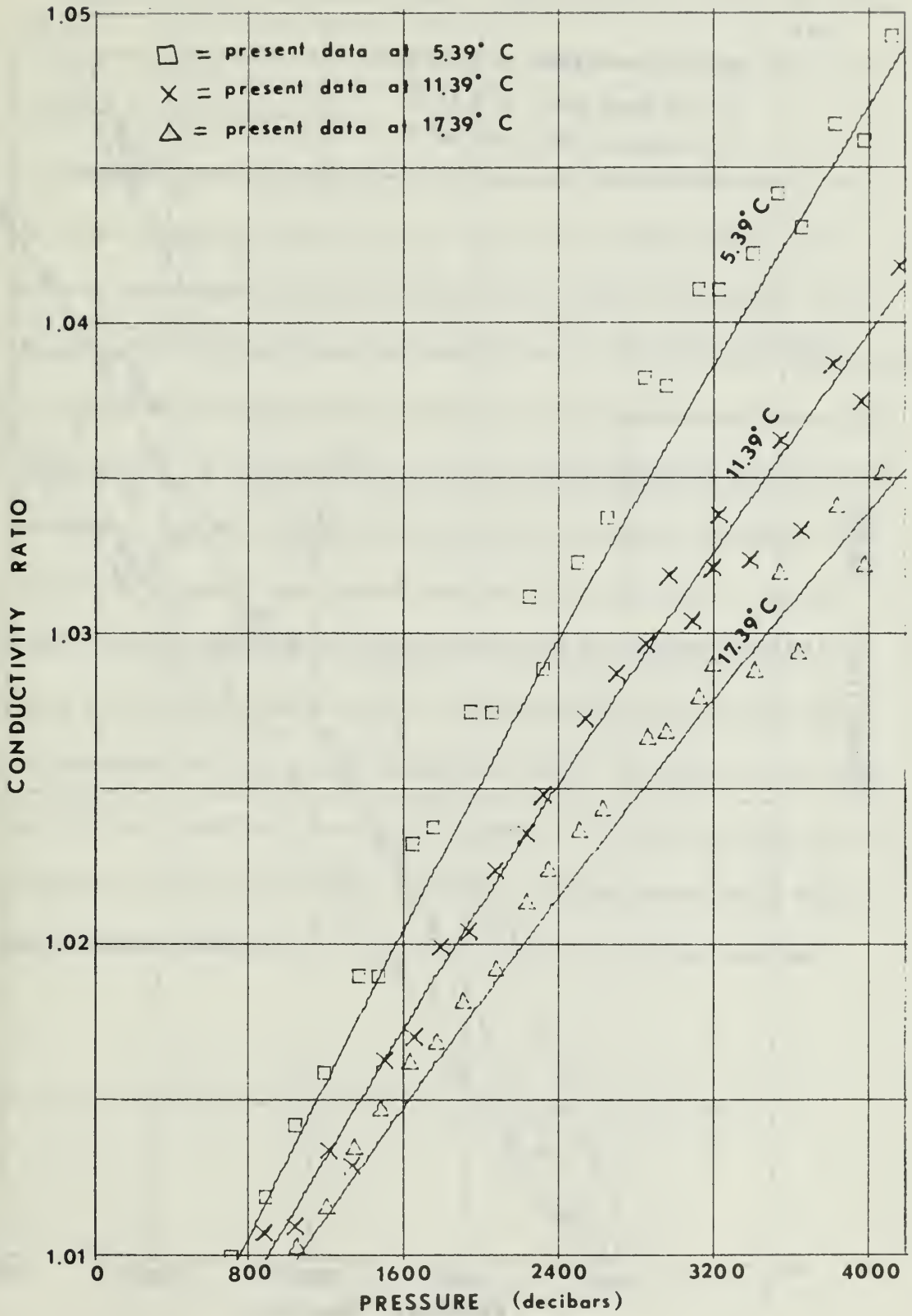

Figure 8a. Conductivity Ratio Vs. Pressure, Salinity 37.152 °/oo; Points - Present Data; Lines - Bradshaw & Schleicher.

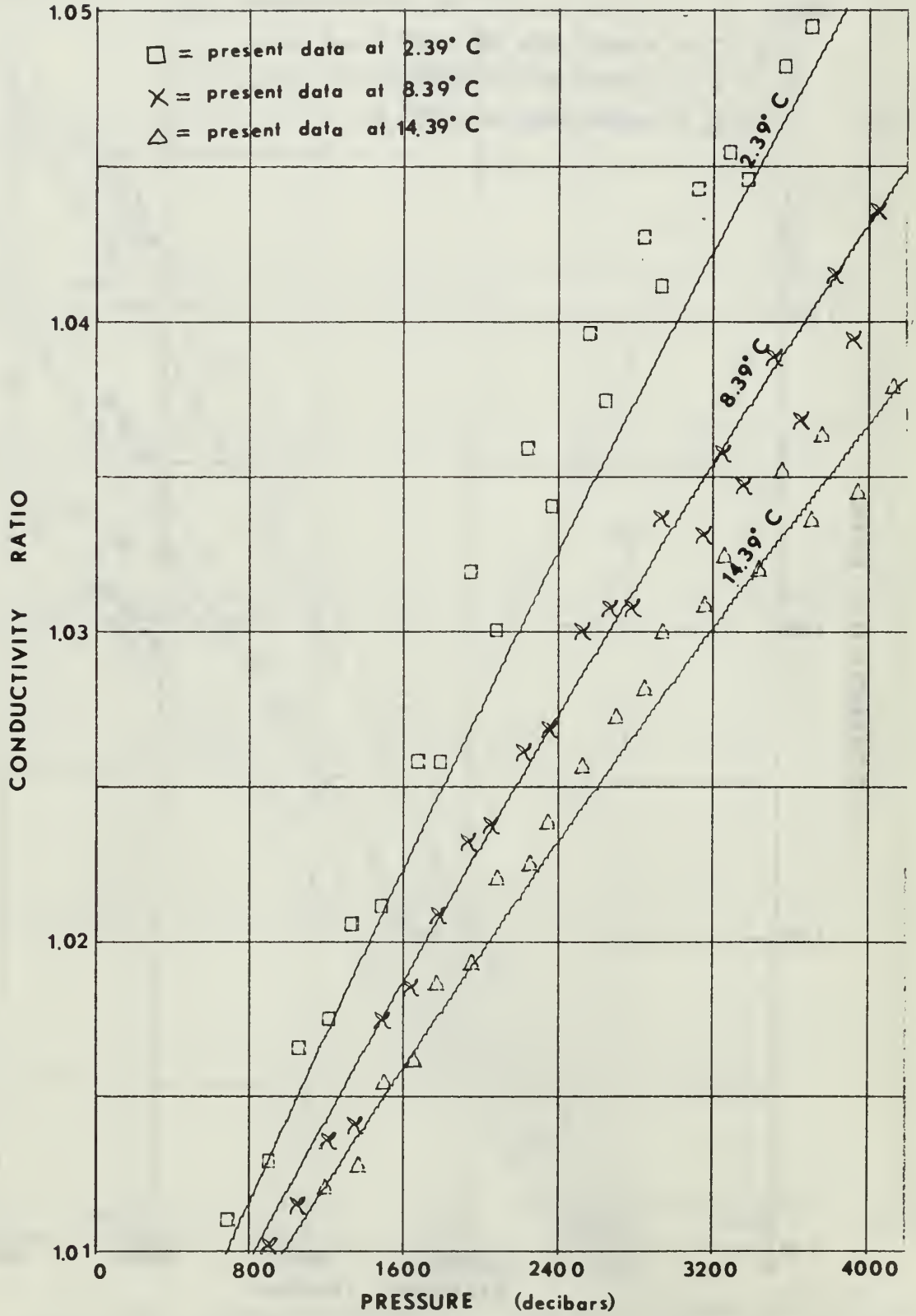

Figure 8b. Conductivity Ratio Vs. Pressure, Salinity 37.152 °/oo; Points - Present Data; Lines - Bradshaw & Schleicher.

Qualitatively, Mays has shown large departures from the linear; occasionally maxima and minima were observed. These were not found in the present study.

Most of the equipment that was used in the present study was the same equipment used by Mays except that modifications were made to permit measuring all parameters more accurately. One important modification was the installation of the thermocouple which permitted measurement of the temperature simultaneously with the conductivity. It was found that changes in the ambient temperature over which this investigator had no control (such as changes in the ventilation system, open doors and dinural temperature change) would cause a significant temperature drift within the vessel. Mays had no way of detecting and compensating for such changes and assumed that the temperature returned to its initial value after the effects of adiabatic heating dissipated. No doubt the gross non-linearities observed by Mays were due to temperature drift within the pressure vessel.

VIII. CORRECTIONS TO SALINITY OR CONDUCTIVITY RATIO

Tables VIII through XII show the total corrections that must be applied when a conductivity ratio is measured at some temperature and pressure and is to be convered to salinity.

A. EQUATIONS UTILIZED

Several equations are needed to generate the tables.

The temperature effect is calculated by using the equation of Brown and Allentoft [1966].

$$(1) \qquad R(BA) = \frac{C(35, T, 0)}{C(35, 15, 0)} = \sum_{n=0}^{4} \left(C_n \times T^n \right)$$

Where $C_o = 0.67652453$

$C_1 = 0.20131661 \times 10^{-1}$

$C_2 = 0.99886585 \times 10^{-4}$

$C_3 = -0.19426015 \times 10^{-6}$

$C_4 = -0.67249142 \times 10^{-8}$

The equation of Bradshaw and Schleicher [1965] was used to describe the pressure effect.

$$(2) \qquad R(BS) = \frac{C(S, T, P)}{C(S, T, 0)} = 1 + 10^{-2} \cdot [\, g \cdot f + h \cdot j \,] \cdot [1 + \ell \cdot m]$$

Where $g = g(T) = 1.5192 - 4.5302 \times 10^{-2} \times T + 8.3089 \times 10^{-4} \times T^2 - 7.900 \times 10^{-6} \times T^3$

$f = f(P) = 1.04200 \times 10^{-3} \times P - 3.3913 \times 10^{-8} \times P^2 + 3.300 \times 10^{-13} \times P^3$

TOP FIGURE IS CORRECTION TO APPLY TO C(S,T,P)/C(35,15,0) TO GET C(S,15,0)/C(35,15,0).

BOTTOM FIGURE IS CORRECTION TO BE APPLIED TO NOMINAL SALINITY (OBTAINED FROM C(S,T,P)/C(35,15,0)) TO GET ACTUAL SALINITY.

TEMP	3	6	9	12	15	18
COND RATIO						
0.65	0.23188 8.7199	0.16259 6.0757	0.10168 3.7784	0.04784 1.7688	0.00001 0.0005	-0.04265 -1.5636
0.70	0.24917 9.4697	0.17475 6.5970	0.10930 4.1020	0.05143 1.9201	0.00002 0.0006	-0.04587 -1.6970
0.75	0.26637 10.2300	0.18686 7.1257	0.11690 4.4300	0.05502 2.0733	0.00002 0.0006	-0.04908 -1.8320
0.80	0.28348 11.0011	0.19893 7.6621	0.12448 4.7628	0.05859 2.2287	0.00002 0.0007	-0.05228 -1.9687
0.85	0.30049 11.7820	0.21095 8.2060	0.13203 5.1003	0.06216 2.3863	0.00002 0.0007	-0.05547 -2.1073
0.90	0.31738 12.5709	0.22290 8.7569	0.13956 5.4425	0.06572 2.5461	0.00002 0.0008	-0.05866 -2.2478
0.95	0.33414 13.3655	0.23479 9.3141	0.14705 5.7893	0.06926 2.7082	0.00002 0.0008	-0.06184 -2.3902
1.00	0.35074 14.1620	0.24660 9.8758	0.15451 6.1400	0.07279 2.8723	0.00002 0.0008	-0.06502 -2.5347
1.05	0.36716 14.9556	0.25832 10.4399	0.16193 6.4939	0.07631 3.0384	0.00002 0.0009	-0.06819 -2.6810
1.10	0.38339 15.7399	0.26995 11.0035	0.16930 6.8496	0.07982 3.2059	0.00002 0.0009	-0.07135 -2.8292
1.15	0.39938 16.5072	0.28146 11.5628	0.17663 7.2056	0.08330 3.3745	0.00002 0.0010	-0.07450 -2.9789
1.20	0.41512 17.2485	0.29284 12.1131	0.18389 7.5598	0.08677 3.5433	0.00003 0.0010	-0.07765 -3.1299

Table VIII. Corrections to Conductivity Ratio or Salinity, Pressure = 0 Decibars.

TOP FIGURE IS CORRECTION TO APPLY TO C(S,T,P)/C(35,15,0) TO GET C(S,15,0)/C(35,15,0).

BOTTOM FIGURE IS CORRECTION TO BE APPLIED TO NOMINAL SALINITY (OBTAINED FROM C(S,T,P)/C(35,15,0)) TO GET ACTUAL SALINITY.

TEMP	3	6	9	12	15	18
COND RATIO						
0.65	0.21925 8.2353	0.15175 5.6652	0.09235 3.4289	0.03978 1.4697	-0.00698 -0.2568	-0.04875 -1.7859
0.70	0.23580 8.9508	0.16325 6.1567	0.09939 3.7266	0.04285 1.5984	-0.00744 -0.2764	-0.05238 -1.9365
0.75	0.25231 9.6777	0.17474 6.6561	0.10642 4.0290	0.04593 1.7293	-0.00790 -0.2959	-0.05599 -2.0887
0.80	0.26876 10.4163	0.18620 7.1637	0.11345 4.3365	0.04901 1.8626	-0.00834 -0.3152	-0.05958 -2.2424
0.85	0.28516 11.1657	0.19764 7.6794	0.12048 4.6491	0.05210 1.9982	-0.00877 -0.3344	-0.06317 -2.3979
0.90	0.30147 11.9247	0.20905 8.2029	0.12750 4.9669	0.05519 2.1364	-0.00918 -0.3535	-0.06673 -2.5552
0.95	0.31770 12.6910	0.22042 8.7335	0.13450 5.2896	0.05829 2.2771	-0.00959 -0.3723	-0.07028 -2.7144
1.00	0.33382 13.4614	0.23175 9.2698	0.14150 5.6168	0.06139 2.4201	-0.00998 -0.3911	-0.07382 -2.8755
1.05	0.34980 14.2313	0.24302 9.8099	0.14848 5.9481	0.06450 2.5655	-0.01037 -0.4096	-0.07734 -3.0383
1.10	0.36562 14.9953	0.25423 10.3512	0.15544 6.2820	0.06761 2.7128	-0.01073 -0.4279	-0.08084 -3.2030
1.15	0.38126 15.7460	0.26535 10.8902	0.16237 6.6172	0.07071 2.8617	-0.01109 -0.4459	-0.08433 -3.3689
1.20	0.39669 16.4749	0.27638 11.4226	0.16927 6.9521	0.07382 3.0115	-0.01144 -0.4635	-0.08779 -3.5359

Table IX. Corrections to Conductivity Ratio or Salinity, Pressure = 1,000 Decibars.

TOP FIGURE IS CORRECTION TO APPLY TO C(S,T,P)/C(35,15,0) TO GET C(S,15,0)/C(35,15,0).

BOTTOM FIGURE IS CORRECTION TO BE APPLIED TO NOMINAL SALINITY (OBTAINED FROM C(S,T,P)/C(35,15,0)) TO GET ACTUAL SALINITY.

TEMP	3	6	9	12	15	18
COND RATIO						
0.65	0.20771 7.7939	0.14185 5.2906	0.08381 3.1094	0.03239 1.1959	-0.01340 -0.4926	-0.05435 -1.9899
0.70	0.22358 8.4777	0.15274 5.7546	0.09031 3.3833	0.03498 1.3038	-0.01429 -0.5304	-0.05836 -2.1564
0.75	0.23944 9.1737	0.16363 6.2269	0.09681 3.6621	0.03758 1.4142	-0.01516 -0.5679	-0.06234 -2.3244
0.80	0.25528 9.8820	0.17454 6.7079	0.10333 3.9462	0.04021 1.5270	-0.01602 -0.6051	-0.06631 -2.4939
0.85	0.27110 10.6021	0.18544 7.1974	0.10987 4.2358	0.04286 1.6424	-0.01684 -0.6421	-0.07025 -2.6650
0.90	0.28687 11.3329	0.19634 7.6954	0.11642 4.5308	0.04552 1.7605	-0.01765 -0.6789	-0.07416 -2.8378
0.95	0.30259 12.0726	0.20722 8.2012	0.12297 4.8312	0.04820 1.8813	-0.01843 -0.7152	-0.07806 -3.0125
1.00	0.31824 12.8180	0.21809 8.7136	0.12954 5.1366	0.05090 2.0047	-0.01920 -0.7514	-0.08193 -3.1890
1.05	0.33380 13.5654	0.22894 9.2311	0.13610 5.4466	0.05362 2.1309	-0.01993 -0.7871	-0.08577 -3.3671
1.10	0.34924 14.3094	0.23974 9.7511	0.14267 5.7600	0.05636 2.2593	-0.02065 -0.8224	-0.08959 -3.5469
1.15	0.36454 15.0435	0.25049 10.2706	0.14923 6.0757	0.05911 2.3898	-0.02134 -0.8572	-0.09339 -3.7280
1.20	0.37966 15.7596	0.26118 10.7858	0.15578 6.3922	0.06187 2.5219	-0.02201 -0.8912	-0.09716 -3.9099

Table X. Corrections to Conductivity Ratio or Salinity, Pressure = 2,000 Decibars.

TOP FIGURE IS CORRECTION TO APPLY TO C(S,T,P)/C(35,15,0) TO GET C(S,15,0)/C(35,15,0).

BOTTOM FIGURE IS CORRECTION TO BE APPLIED TO NOMINAL SALINITY (OBTAINED FROM C(S,T,P)/C(35,15,0)) TO GET ACTUAL SALINITY.

TEMP	3	6	9	12	15	18
COND RATIO						
0.65	0.19719 7.3922	0.13280 4.9491	0.07601 2.8178	0.02563 0.9456	-0.01928 -0.7085	-0.05949 -2.1769
0.70	0.21243 8.0469	0.14313 5.3879	0.08200 3.0696	0.02777 1.0344	-0.02057 -0.7630	-0.06385 -2.3581
0.75	0.22769 8.7143	0.15348 5.8352	0.08802 3.3268	0.02994 1.1257	-0.02183 -0.8170	-0.06818 -2.5406
0.80	0.24296 9.3945	0.16386 6.2916	0.09407 3.5893	0.03214 1.2198	-0.02306 -0.8708	-0.07248 -2.7245
0.85	0.25823 10.0875	0.17426 6.7569	0.10015 3.8576	0.03438 1.3165	-0.02426 -0.9241	-0.07675 -2.9101
0.90	0.27350 10.7921	0.18468 7.2312	0.10625 4.1316	0.03664 1.4161	-0.02543 -0.9771	-0.08099 -3.0973
0.95	0.28874 11.5066	0.19512 7.7140	0.11239 4.4113	0.03894 1.5185	-0.02656 -1.0298	-0.08520 -3.2862
1.00	0.30395 12.2287	0.20556 8.2041	0.11855 4.6964	0.04127 1.6238	-0.02766 -1.0820	-0.08938 -3.4769
1.05	0.31910 12.9545	0.21599 8.7003	0.12473 4.9866	0.04363 1.7321	-0.02873 -1.1337	-0.09353 -3.6692
1.10	0.33417 13.6794	0.22641 9.2002	0.13093 5.2809	0.04601 1.8430	-0.02977 -1.1848	-0.09765 -3.8631
1.15	0.34913 14.3970	0.23681 9.7013	0.13714 5.5784	0.04843 1.9564	-0.03078 -1.2351	-0.10173 -4.0581
1.20	0.36396 15.0999	0.24718 10.1998	0.14336 5.8775	0.05087 2.0719	-0.03174 -1.2844	-0.10578 -4.2539

Table XI. Corrections to Conductivity Ratio or Salinity, Pressure = 3,000 Decibars.

TOP FIGURE IS CORRECTION TO APPLY TO C(S,T,P)/C(35,15,0) TO GET C(S,15,0)/C(35,15,0).

BOTTOM FIGURE IS CORRECTION TO BE APPLIED TO NOMINAL SALINITY (OBTAINED FROM C(S,T,P)/C(35,15,0)) TO GET ACTUAL SALINITY.

TEMP	3	6	9	12	15	18
COND RATIO						
0.65	0.18762 7.0272	0.12456 4.6383	0.06888 2.5519	0.01944 0.7170	-0.02467 -0.9059	-0.06419 -2.3481
0.70	0.20228 7.6552	0.13436 5.0539	0.07441 2.7836	0.02118 0.7883	-0.02632 -0.9756	-0.06888 -2.5427
0.75	0.21697 8.2963	0.14421 5.4783	0.07998 3.0208	0.02295 0.8623	-0.02794 -1.0450	-0.07353 -2.7386
0.80	0.23171 8.9508	0.15411 5.9120	0.08559 3.2635	0.02476 0.9389	-0.02952 -1.1138	-0.07814 -2.9359
0.85	0.24648 9.6185	0.16405 6.3550	0.09125 3.5122	0.02661 1.0185	-0.03105 -1.1823	-0.08272 -3.1346
0.90	0.26127 10.2987	0.17402 6.8074	0.09695 3.7668	0.02851 1.1010	-0.03255 -1.2503	-0.08726 -3.3351
0.95	0.27607 10.9900	0.18403 7.2688	0.10270 4.0274	0.03045 1.1866	-0.03401 -1.3178	-0.09176 -3.5372
1.00	0.29086 11.6900	0.19407 7.7382	0.10848 4.2938	0.03243 1.2752	-0.03543 -1.3849	-0.09623 -3.7409
1.05	0.30562 12.3954	0.20413 8.2145	0.11430 4.5656	0.03446 1.3669	-0.03681 -1.4512	-0.10066 -3.9463
1.10	0.32034 13.1019	0.21420 8.6958	0.12015 4.8421	0.03652 1.4616	-0.03815 -1.5170	-0.10505 -4.1531
1.15	0.33499 13.8036	0.22426 9.1793	0.12604 5.1225	0.03863 1.5591	-0.03944 -1.5817	-0.10940 -4.3610
1.20	0.34953 14.4935	0.23431 9.6619	0.13194 5.4053	0.04077 1.6591	-0.04069 -1.6453	-0.11371 -4.5696

Table XII. Corrections to Conductivity Ratio or Salinity, Pressure = 4,000 Decibars.

$$h = h(P) = 4.0\times10^{-4} + 2.577\times10^{-5}\times P - 2.492\times10^{-9}\times P^2$$

$$j = j(T) = 1.000 - 1.535\times10^{-5}\times T + 8.276\times10^{-3}\times T^2 - 1.657\times10^{-4}\times T^3$$

$$\ell = \ell(T) = 6.950 \times 10^{-3} - 7.6\times10^{-5}\times T$$

$$m = m(S) = 35.00 - S$$

Two equations now used to define salinity by UNESCO were taken from the International Oceanographic Tables [1966]. The first converts a conductivity ratio measured at some temperature (T) to one measured at 15°C.

$$(3)\quad R(15) = \frac{C(S, 15, 0)}{C(35, 15, 0)} = R(ZO) + 10^{-5}\left[R(ZO)\cdot\{R(ZO) - 1\}\cdot\{T - 15\}\right]\cdot \left[96.7 - 72.0\cdot R(ZO) + 37.3\cdot R(ZO)^2 - \{0.63 + 0.21\cdot R(ZO)^2\}\{T - 15\}\right]$$

$$\text{Where}\quad R(ZO) = \frac{C(S, T, O)}{C(35, T, O)}$$

The second equation defines salinity in terms of R(15).

$$(4)\quad S = \sum_{n=0}^{5}\left(C_n \times R(15)^n\right)$$

Where $C_o = -0.08996$

$C_1 = 28.29720$

$C_2 = 12.80832$

$C_3 = -10.67869$

$C_4 = 5.98624$

$C_5 = -1.32311$

B. METHOD OF GENERATION OF CORRECTIONS

First a $R(TP) = \frac{C(S, T, P)}{C(35, 15, 0)}$ was selected and a nominal salinity was calculated from it using equation (4).

Next, $R(BA) = \frac{C(35, T, O)}{C(35, 15, O)}$ was calculated from equation (1). R(TP) was then divided by R(BA) to get R(ZP).

$$R(ZP) = \frac{C(S, T, P)}{C(35, 15, 0)} \Big/ \frac{C(35, T, 0)}{C(35, 15, 0)} = \frac{C(S, T, P)}{C(35, T, 0)}$$

Then R(BS) is calculated using equation (2). Since the salinity is unknown, the nominal salinity calculated from R(TP) is used as a first estimate of salinity. R(ZP) was divided by R(BS) to get R(ZO).

$$R(ZO) = \frac{C(S, T, P)}{C(35, T, 0)} \Big/ \frac{C(S, T, P)}{C(S, T, 0)} = \frac{C(S, T, 0)}{C(35, T, 0)}$$

R(ZO) is then convered to R(15) by using equation (3). R(15) was then converted to a second estimate of salinity with equation (4).

This second estimate of salinity was used in equation (2) and the process was repeated to get a third estimate of salinity. New salinity estimates were generated by this iterative process until two successive estimates differed by less than 0.0001 °/oo. The difference between the final salinity estimate and the nominal salinity is the salinity correction. The difference between the final R(15) and R(TP) is the conductivity ratio correction.

C. USE OF CORRECTIONS

The tables may be used in one of two ways. The conductivity ratio may be corrected and the result converted to salinity using equation (4) or the International Oceanographic Tables; or, alternately, the conductivity ratio may be converted to salinity first and then the salinity may be corrected. Both corrections are never applied since they are equivalent; one being in terms of conductivity ratio -- the other in terms of salinity.

Tables VIII through XII, in which R(TP), temperature and pressure are incremented in very large steps, are not meant to be working tables but are only to show the magnitude of the corrections. Working tables with small increments of R(TP), temperature and pressure could be generated in the same manner. Also, individual observations of R(TP), temperature and pressure could be converted to salinity with a computer program. The latter method is most efficient for processing large volumes of data and is now used by General Dynamics Convair Division in the ONR "Monster Buoy" system [Kenneth Samples, personal communication]. The method is described in an unpublished report by N. P. Fofonoff of Woods Hole Oceanographic Institution entitled "Conversion of Conductivity to Salinity."

IX. EXPLANATION OF PRESSURE EFFECT

The increase in specific conductance was found to be due to three effects of about the same magnitude. These are: increased effective concentration due to compression, increased ionic mobility due to the breakdown of Frank-Wen clusters and the increased dissociation of magnesium sulphate ion pairs.

A. INCREASED EFFECTIVE CONCENTRATION DUE TO COMPRESSION

When a given parcel of sea water containing a certain number of ions is subjected to pressure, its volume will decrease. The number of ions, however, will remain the same; and, in effect, the concentration will be increased. This will result in increased specific conductance.

The equation of state for sea water according to Tumlirz was used to estimate this effect. The equation of state is discussed by Fofonoff [1962] and Eckart [1958]. The increased specific conductance was assumed to be inversely proportional to the relative volume decrease and was estimated using:

$$C(P) = \left(\frac{\alpha(1)}{\alpha(P)} \right) \times C(1)$$

Where:

$C(P)$ = Estimate of increased specific conductance at a pressure (P) due to increased effective concentration.

$\alpha(1)$ = Specific volume at atmospheric pressure.

$\alpha(P)$ = Specific volume at pressure (P).

C(1) = Specific conductance at atmospheric pressure.

The estimate of the change in specific conductance due to increased effective concentration was subtracted from the observed specific conductance at each data point; the residues were then plotted. If the residues were nearly constant so that their plot was about horizontal, then the increased specific conductance would be entirely due to increased effective concentration.

The original data points corrected to 18°C (C) and the residues, after subtracting out the effect of increased effective concentration (C-A), were plotted as squares and triangles respectively and are shown in Figures 9 and 10. As may be seen, the increased effective concentration does not explain the entire conductivity change and other processes must be at work. At the lower temperatures studied, this effect decreased slightly since sea water is less compressible at lower temperatures.

B. INCREASED IONIC MOBILITY DUE TO BREAKDOWN OF FRANK-WEN CLUSTERS

Water, at ambient temperatures, contains ice-like structures often called polmers or Frank-Wen clusters. These clusters were described by Frank and Wen [1957] and they produce many of the anomalous features of water.

The Frank-Wen clusters are made up of several (up to 8 or 10) water molecules joined by a semi-covalent hydrogen bond. The

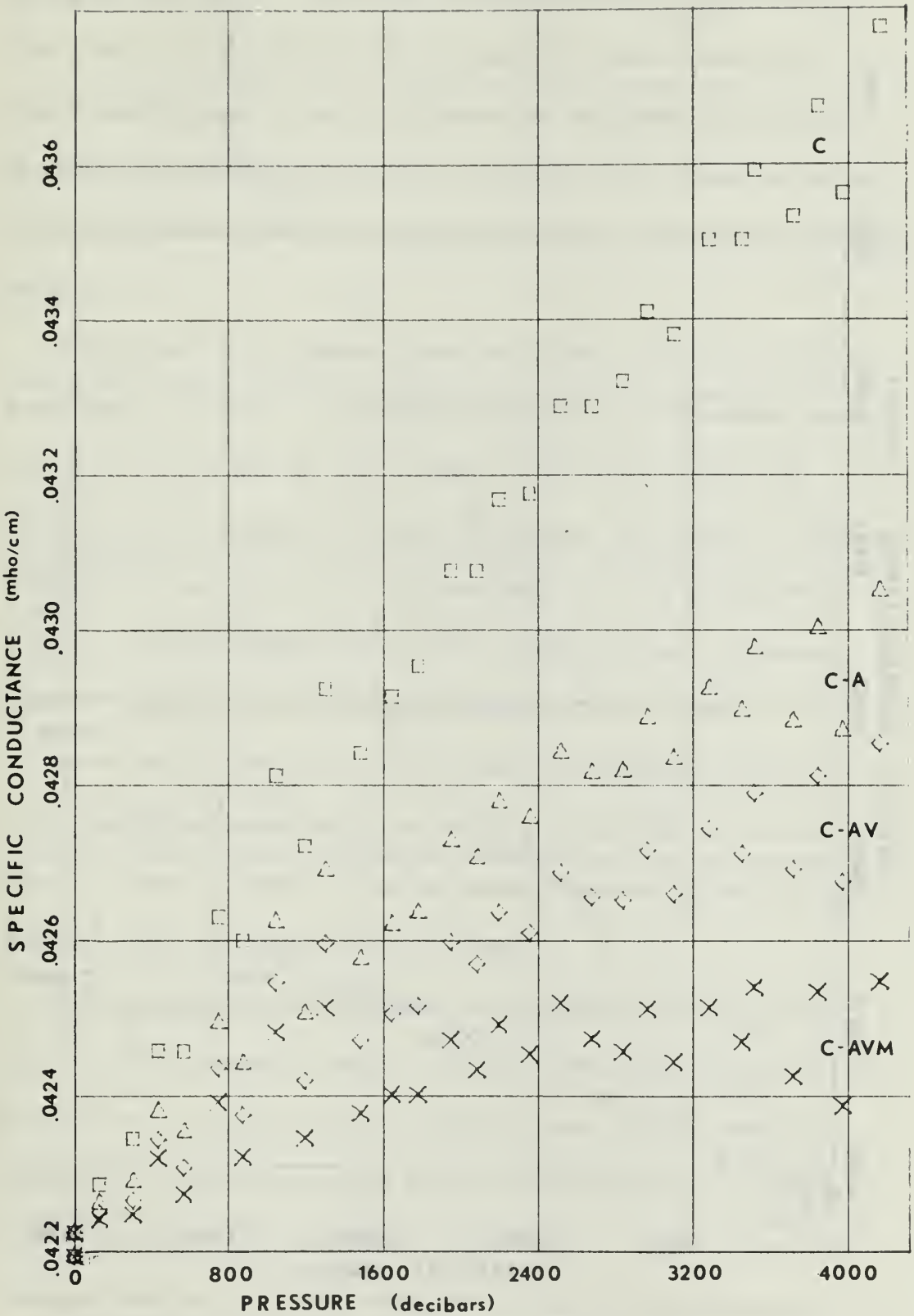

Figure 9. Analysis of Pressure Effect on Specific Conductance, Salinity 32.448 °/oo, Temperature 18.0°C.

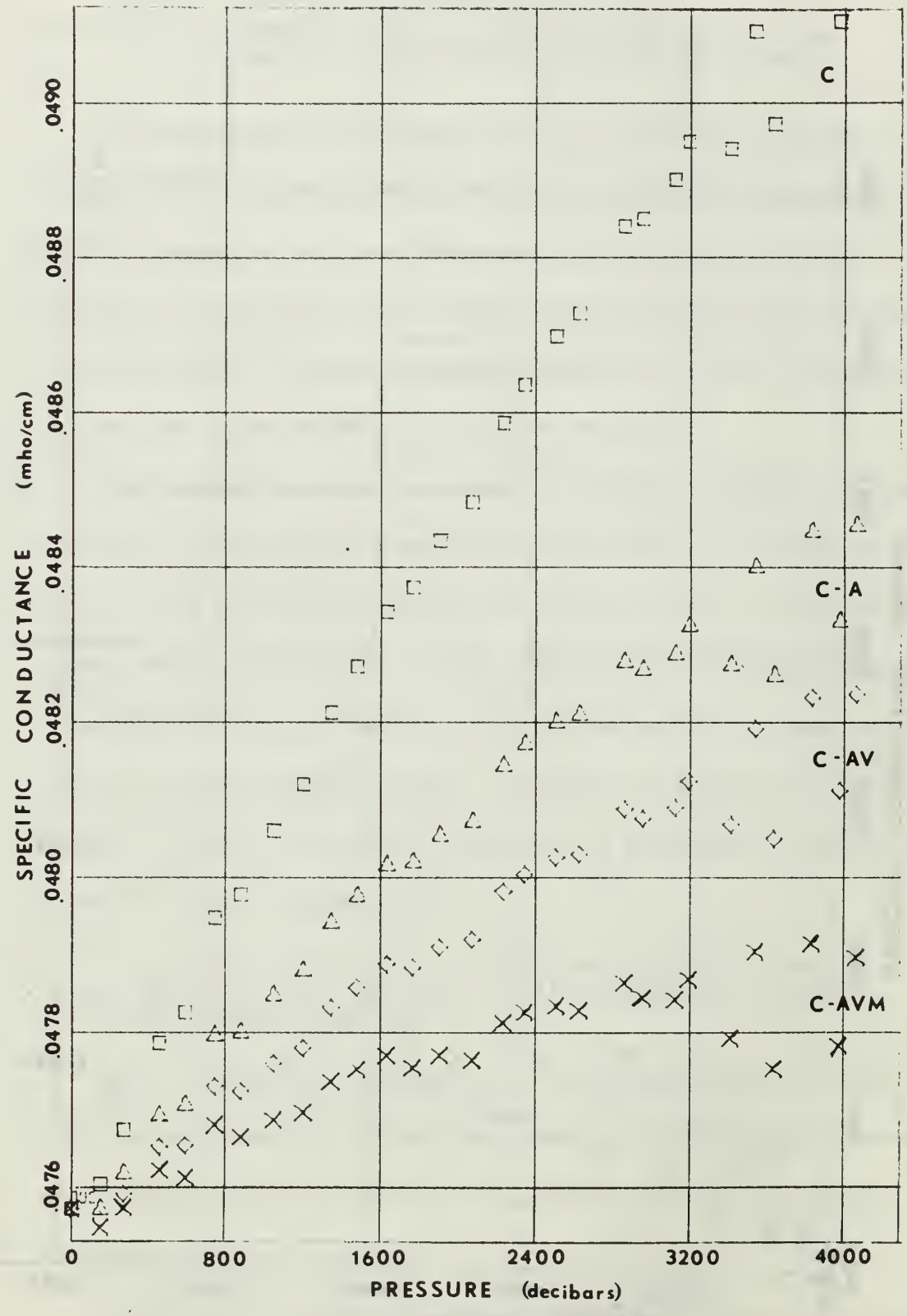

Figure 10. Analysis of Pressure Effect on Specific Conductance, Salinity 37.152 °/oo, Temperature 18.0°C.

clusters are termed "flickering" in that they form and dissolve with a half life of about 10^{-10} sec; however, this is sufficiently long enough to have a meaningful effect on the physical properties of water [Frank and Wen, 1957]. In view of this, references to the number of Frank-Wen clusters present must be taken in a statistical sense.

The Frank-Wen clusters, because of their bonding, are less dense than bulk water. Increased temperature or increased pressure will break down the Frank-Wen clusters and reduce their number. In the ranges of interest in the sea, the effect of pressure is greater by far since at 10,000 decibars all of the Frank-Wen clusters are destroyed while at 100^{o}C and atmospheric pressure there is an appreciable fraction remaining [Horne, 1968].

A decrease in the number of Frank-Wen clusters will result in increased molecular and ionic mobility along with decreased volume. This accounts for the anomalous decrease in the viscosity of water when the pressure is increased.

The physical analogy between an ion passing through a fluid and a particle passing through a viscous continuum as described by Stokes Law is crude; however, Walden's Rule derived from this analogy has wide experimental validity particularly for a given solvent [Moore, 1955; MacInnes, 1939; Kortum, 1962]. One may conclude that they are both controlled by the same mechanism, i.e., the breakdown of Frank-Wen clusters. That there should be a

correlation between reduced viscosity and increased conductivity is intuitively appealing as well as experimentally demonstrable. Thus, the effect of the change in specific conductance due to the breakdown of Frank-Wen clusters may be estimated by using the change in viscosity. The results of Horne and Johnson [1966b] for the viscosity of compressed sea water were used in the following equation:

$$CV(P) = \left(\frac{\eta(1)}{\eta(P)} \right) \times C(P)$$

Where

CV(P) = Estimate of increased specific conductance at a pressure (P) due to increased effective concentration and Frank-Wen cluster breakdown.

η (1) = Viscosity at atmospheric pressure.

η (P) = Viscosity at pressure (P).

C(P) = Estimate of increased specific conductance at a pressure (P) due to increased effective concentration.

The estimate of the change in specific conductance due to increased effective concentration and Frank-Wen cluster breakdown was subtracted from the observed specific conductance at each data point; the new residues (C-AV) were then plotted as diamonds and are shown in Figures 9 and 10. Although both effects are significant, the change in specific conductance is still not completely explained.

At lower temperatures, the effect of Frank-Wen cluster breakdown becomes larger until at 3°C it is greater than the effect of

increased effective concentration. This is what one would expect since, for a given pressure, there are more Frank-Wen clusters present at lower temperatures. Thus, at lower temperatures, an incremental pressure increase will break down more Frank-Wen clusters and produce a correspondingly larger increase in specific conductance.

C. INCREASED DISASSOCIATION OF MAGNESIUM SULPHATE

All of the ionic constituents of sea water are strong electrolytes which do not form ion pairs with the exception of magnesium sulphate. The strong electrolytes are, for practical purposes, completely free ions at the temperatures and pressures found in the ocean. That is, they are completely disassociated into charged ions all of which participate in the conduction process. Magnesium sulphate is only partly disassociated and only part of the magnesium and sulphate molecules are present as separate charged ions; the remainder are present as ion pairs that are electrically neutral and do not participate in the process of conduction. When the pressure is increased, some of the electrically neutral ion pairs will break down or disassociate into charged ions that will participate in the conduction process. Thus, increased pressure will increase the number of magnesium sulphate ions present thereby increasing the specific conductance.

The disassociation and association of magnesium sulphate with the passage of a sonic pressure wave will absorb energy from the

pressure wave. This explains the unusually large sound absorption in sea water compared to fresh water [Fisher, 1958; Urick, 1967].

The increase in the equivalent molar conductance of dilute magnesium sulphate solutions at 25°C has been determined by Fisher [1962]. Literature which reports the temperature effect on the conductivity of magnesium sulphate or which describes the effect of temperature on the association constants of magnesium sulphate could not be located in time to be used in this analysis. The work of Simpson [1966] may provide this information. Consequently, Fisher's data at 25°C was used with the present data at 18°C to estimate the role played by the increased disassociation of magnesium sulphate in increasing the specific conductance of sea water when the pressure is increased.

The magnesium sulphate concentration in the sea water samples studied was calculated to be 0.026 M and 0.030 M. The values of the relative equivalent molar conductance (Λ_{500}/Λ_1) for these concentrations were extrapolated from Fisher's data. The relative equivalent molar conductances were converted to relative specific conductances (κ_{500}/κ_1) by

$$\frac{\kappa_{500}}{\kappa_1} = \frac{\Lambda_{500}}{\Lambda_1} \cdot \frac{\alpha(1)}{\alpha(500)}$$

Where:

Λ_{500} = Equivalent molar conductance at 500 atm.

Λ_1 = Equivalent molar conductance at atmospheric pressure.

$\alpha_{(500)}$ = Specific volume at 500 atm.

$\alpha_{(1)}$ = Specific volume at atmospheric pressure.

K_{500} = Specific conductance at 500 atm.

K_1 = Specific conductance at atmospheric pressure.

The relative specific conductance is then substituted in the formula

$$CM(P) = \left[\frac{P}{500} \times \left(\frac{K_{500}}{K_1} - 1 \right) + 1 \right] \times K_1$$

Where:

CM(P) = Estimate of the increased specific conductance of magnesium sulphate at a pressure (P) due to increased disassociation.

P = Pressure in atmospheres.

K_1 = Specific conductance of magnesium sulphate at atmospheric pressure extrapolated from Fisher [1962].

These estimates of increased specific conductance were made for magnesium sulphate solutions that had the same concentration as the magnesium sulphate in the sea water samples studied. Consequently, the change in the specific conductance of the sea water due to the disassociation of magnesium sulphate may be expected to be the same as the change in the specific conductance of the magnesium sulphate solutions.

The estimate of the change in specific conductance due to the increased disassociation of magnesium sulphate was subtracted

from the residues that remained after the two previous effects had been subtracted from the original data points. The new residues (C-AVM), which represent the original data points corrected for the effect of increased effective concentration, Frank-Wen cluster breakdown and increased disassociation of magnesium sulphate, were plotted as crosses and are shown in Figures 9 and 10.

These three effects account for well over 80% of the change in the specific conductance of sea water with pressure and may be considered the major effects. The remaining unexplained portion may be due to the interaction of these three effects, errors in estimating these three effects or to a fourth as yet unknown effect.

It should be remembered that the effect of the increased disassociation of magnesium sulphate plotted on the graphs for $18^{o}C$ was calculated from Fisher's data at $25^{o}C$. If it were possible to calculate this effect at $18^{o}C$, it is believed that the resulting effect would be slightly smaller than the effect calculated from Fisher's data at $25^{o}C$ for the following reasons.

First, with lower temperature, the increased effective concentration effect decreases slowly while the Frank-Wen cluster breakdown effect increases rapidly. Thus the remaining part, to be explained by increased magnesium sulphate disassociation or any other effect, decreases with decreasing temperature.

Secondly, the magnesium sulphate disassociation may be compared with the Frank-Wen cluster breakdown in water, but some

differences must be noted. In both cases, there is a bonding to form a polmer or ion pair from free disassociated molecules or ions. Also, either type of bonding is encouraged by decreasing temperature and discouraged by increasing pressure. In contrast, the magnesium sulphate is strongly associated while the water is very weakly associated, i.e., much of the magnesium sulphate is in the form of ion pairs and little is in the form of free ions while water, at normal temperatures, is mostly bulk water with a small amount of polmerization. This is because the enthalpy of disassociation for magnesium sulphate is quite high while for Frank-Wen clusters it is low. Thus, in the case of Frank-Wen cluster breakdown, pressure is the dominant factor; but, in magnesium sulphate disassociation, temperature is the dominant factor and this effect becomes less important at lower temperatures.

In summary, at the higher temperatures studied, the effect of increased effective concentration is most important while both Frank-Wen cluster breakdown and increased disassociation of magnesium sulphate effects are moderately important. At the lower temperatures studied, the effect of Frank-Wen cluster breakdown increases to become the most important while both the increased effective concentration and increased disassociation of magnesium sulphate effects become smaller.

X. CONCLUSIONS AND RECOMMENDATIONS

Although the effect of pressure on the specific conductance of sea water is nearly linear, it must be described by a higher order polynomial if it is to be used to measure salinity to the usual accuracy required in oceanography.

Past studies in which the temperature of the sample was not measured simultaneously with the specific conductance resulted in data with large scatter or other anomalies. Any further study should provide for measurement of the temperature within the pressure vessel with an accuracy of 0.001°C or better.

The best description of the effect of pressure of the conductivity of sea water presently available is the equation derived by Bradshaw and Schleicher [1965]. This equation may be used to compile correction tables or it may be used in an appropriate computer program.

The three major effects that cause the increase in specific conductance of sea water with increased pressure are: increased effective concentration due to compression, increased ionic mobility due to the breakdown of Frank-Wen clusters and the increased disassociation of magnesium sulphate ion pairs. It is not clear whether or not there are other effects present.

For future work, a more detailed study of magnesium sulphate under pressure is recommended. A check on the effect of added

ionic strength on the disassociation of magnesium sulphate would be useful. The determination of the temperature coefficients of specific conductance at elevated pressures is also recommended.

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13. ABSTRACT

The increase in specific conductance of sea water with increased pressure was measured using two parcels of sea water (32.448 °/oo and 37.152 °/oo) at six temperatures from 2.39°C to 17.39°C. The pressure was incremented in steps of 140 decibars to a pressure of 4,000 decibars. Although the effect of pressure on the specific conductance of sea water is nearly linear, it must be described by a higher order polynomial if it is to be used to measure salinity to the usual accuracy required in oceanography. The three major effects that cause the increase in the specific conductance of sea water with increased pressure are shown to be: increased effective concentration due to compression, increased ionic mobility due to the breakdown of Frank-Wen clusters and the increased disassociation of magnesium sulphate ion pairs.

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